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PHOSPHORUS RELEASE FROM LAKE SEDIMENTS

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Battelle-Pacific Northwest Laboratories

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PHOSPHORUS RELEASE FROM LAKE SEDIMENTS

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ABSTRACT

The principal objectives of these investigations were to chemically define the major forms of phosphorus (P) in sediments of Upper Klamath Lake, Oregon, determine the potential for release of P from the sediment as influenced by water and sediment composition and environmental parameters, and establish the relationship between P release and algal growth.

Methods were developed for the characterization of inorganic and organic P components and for measurement of P release from sediments and subsequent availability to algae. Sediment characterization was extended to other lake systems including Shagawa Lake in Minnesota, Agency and Diamond Lakes in Oregon and Lake Erie.

Sediments of Upper Klamath Lake, although differing in their ability to release P, exhibited seasonal changes in P concentration. These changes were most pronounced in the inorganic P fraction and in a bay which received agricultural runoff and initially contained relatively large quantities of P in the sediment interstitial water. Release of and resorption of P associated with the solid phase occurred. Release appeared to be largely from non-occluded Fe-P whereas resorption was primarily in the form on non-occluded Al-P. The rate and extent of P release, described by regression models, was related to sediment composition. Release was accelerated by temperature and the presence of a P sink such as an anion exchange resin. Evidence obtained in the field suggested that actively reproducing phytoplankton may also serve as a P sink increasing P release. Algal growth response to P released from sediments during dialysis was approximately equivalent to the response to orthophosphate.

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SECTION I

SUMMARY AND CONCLUSIONS

The principal objectives of these investigations were to (*i*) chemically define the predominant inorganic and organic forms of P in sediments in Upper Klamath Lake, Oregon, (*ii*) determine the potential for release of soluble P from the solid phase with changes in temperature, pH and water and sediment composition, (*iii*) establish the relationship between P release and algal growth and (*iv*) develop suitable methods for accomplishing the above. These methods were also applied to Shagawa Lake in Minnesota, Agency Lake and Diamond Lake in Oregon and Lake Erie (summarized in the Appendix).

The Upper Klamath Lake studies were undertaken in several phases based on the original objectives. These included (*i*) development of methods for measurement of total, inorganic and organic sediment P and for characterization of sediment P mineral and organic components (Section IV A, B), (*ii*) examination of sediments that changed with limnological conditions to determine the most labile P mineral or organic components (Section IV B), and (*iii*) laboratory studies to develop methods for measurement of the potential for sediment P release and to verify the changes in sediment chemistry postulated from analysis of field samples (Section V).

DEVELOPMENT OF METHODS FOR MEASUREMENT OF SEDIMENT PHOSPHORUS

In initial testing of methods for measurement of the forms of sediment P, total sediment P determined by Na_2CO_3 fusion, HCl-NaOH extraction and high temperature ignition methods generally agreed within 8%, approximating field sampling variation. However, high temperature ignition methods consistently underestimated total P compared to the other methods, evidently due to the presence of P in mineral-occluded forms which were not subject to extraction after ignition.

Estimates of inorganic sediment P using H_2SO_4 extraction and the summation of inorganic P fractions representing various forms of Al and Fe-P measured by serial extraction of the sediments were not significantly different. For routine measurements of inorganic P potentially available to solution in Upper Klamath Lake systems, the simpler H_2SO_4 extraction method was employed. In cases in which more definitive information was required regarding the forms of inorganic P present, the serial extraction scheme was employed.

The sediment organic material was fractionated into benzene-ethanol soluble, humate (alkali soluble, acid insoluble) and fulvate (alkali soluble, acid soluble) components. The fulvate fraction was further characterized by separation into 5 fractions based on extractability after concentration on activated C. A method was developed for measurement of inositol hexaphosphate in sediment extractives.

Organic C in benzene-ethanol, humate and fulvate fractions ranged from 65.0 to 83.2% of total sediment organic C content. Organic P in these fractions ranged from 36.8 to 51.2% of sediment organic P content. Little organic P was subject to hydrolysis by the solvents employed and the nonextractable fraction must be considered quite stable chemically and microbiologically, contributing little to P release from sediments. Inositol hexaphosphate was not detectable (< 10 μg/g) in Upper Klamath Lake sediments.

PHOSPHORUS STATUS OF SEDIMENTS AS RELATED TO CHANGES IN LIMNOLOGICAL CONDITIONS

Limnological conditions and their relationship to changes in sediment P status differed with lake location. Seasonal changes in sediment composition were most pronounced at a lake location which received agricultural runoff waters and where maximum biological activity occurred as reflected in increased surface water organic C and N, turbidity and phytoplankton growth. At this location, total sediment P decreased sharply during the late spring and early summer corresponding to the period of exponential growth of the lake phytoplankton population. During the late summer and early fall when plankton growth entered the stationary and declination phases, sediment organic C, total N, and P increased, evidently as a result of the deposition of detritus containing these elements. Combining data from all locations, changes in sediment inorganic P were negatively correlated to surface water organic C. Inorganic P appeared to account for most of the variation in total P. However, some mineralization of organic C and N occurred, and changes in total sediment P were highly correlated to changes in sediment organic C and N.

Sediments exhibiting seasonal changes in distribution of total, inorganic and organic P during a single season were further examined to determine if observed changes could be attributed to specific inorganic and organic chemical fractions. In general it appeared that P soluble in 0.1 N NaOH, taken as non-occluded Fe-P, accounted for most of the reduction in inorganic P, whereas increases in inorganic P were due primarily to increases in NH_4F-soluble P taken as non-occluded Al-P. Considering data from all lake locations during the year, P soluble in chemical extractions taken to represent forms of Al-P, Fe-P and Fe and Al oxide occluded P accounted for approximately 85% of the changes occurring throughout a 1-year sampling period.

Measurement of the distribution of organic C in sediment organic extracts from a single location sampled seasonally indicated that the major portion of extractable organic C was in the fulvic acid fraction. The major portion of fulvic acid C was present in higher molecular weight substances. The C contents of the fulvate and humate fractions, relatively resistant to microbial attack, were not related to changes in sediment organic C which took place during the monitoring period. However, organic C in the benzene-ethanol fraction varied with changes in sediment organic C. Organic materials likely contained in this fraction, i.e. lipids, fats and waxes derived from fresh or relatively undecomposed organic detritus should serve as available energy sources for the sediment microfloral population under conditions of increased temperature in the spring. As phytoplankton growth in surface waters declines in late summer, the rate of deposition of these materials may exceed the rate of decomposition resulting in an increase in sediment concentration.

Because approximately 50% of the sediment organic P consisted of highly stable materials not soluble in the solvents employed, changes in sediment organic P would not be attributed definitively to a single fraction. However, it is noteworthy that as in the case of organic C, the fulvate fraction contained the highest concentration of the recovered sediment organic P. In contrast to sediment organic C, the largest proportion of fulvic acid organic P was present in water soluble fractions of relatively low molecular weight. Water soluble, and likely the most labile, fulvate fractions and the benzene-ethanol fractions varied on an absolute basis with seasonal changes in sediment organic P. If it is necessary to predict changes in sediment organic P it would appear that these fractions would be a useful point of departure for future research.

LABORATORY STUDIES OF THE POTENTIAL FOR P RELEASE FROM SEDIMENTS

Although gross changes in sediment P composition occurred at one location during the field phase of the program, it was recognized from the onset of the program that, due to the high concentration of P in the sediment relative to the lake water, gross changes in sediment P status need not occur in order for sediments to significantly influence water composition. Therefore laboratory studies were undertaken to define more precisely the rate and extent of P release from sediments. Several methods were developed and preliminarily tested with respect to their ability to allow (*i*) separate manipulation of sediment and water parameters (*ii*) measurement of the kinetics of P release as well as the potential for P release and (*iii*) evaluation of the algal growth potential of released P. Prototypic methods included a dialysis method involving equilibration of sediment in cellulose acetate membrane tubing with water, a dialysis method in which sediment and water in glass half-cells were partitioned with a 0.45 μ filter and a sediment-resin equilibration system (Section V A). These tests were evaluated as to optimum conditions for P release and utilized in subsequent studies of the factors influencing the P status of lake sediment (Section V B).

Field studies indicated that inorganic P fractions were primarily responsible for seasonal changes in sediment P content. These changes were related to biological action by the surface waters and at one location the surface water temperature. In the laboratory studies emphasis was therefore accorded the effects of P sinks in the forms of an anion exchange resin and algal growth, and on temperature as these may have effected changes in sediment inorganic P. Simple and multiple regression models were devised which described the rate of P release from sediments as a function of time, temperature and sediment composition. The results of the release studies were related to algal growth potential using the EPA provisional bioassay.

Several general conclusions may be drawn from the P release studies using the filter dialysis system. In general, the quantity of P released to solution increased with incubation time to 90 days. Inorganic P generally constituted the major portion of P released to solution. Differences in the rate and extent of P release in the dialysis systems reflected differences in total sediment P and interstitial water P concentration. However, if P present in the interstitial waters was subtracted from total P release in the dialysis system, it could be concluded that similar quantities of P, amounting to approximately 12% of total inorganic P, were released from the solid phase of sediments from all locations.

As in the case of sediment sampled during the field phase, chemical extracts representing forms of Al-P and Fe-P appeared to account for most of the variation in sediment inorganic P during laboratory incubation. Reductions in 0.1 M NaOH-extractable P, representing non-occluded Fe-P forms, were most consistently responsible for decreases in sediment inorganic P. Increases in inorganic P, when observed, were generally associated with increases in the NH_4F extract representing non-occluded Al-P forms. Experiments designed to measure sorption of ^{32}P spiked into the water half-cell during sediment dialysis tended to substantiate this phenomenon. The major portion of ^{32}P sorbed was in the NH_4F fraction. Temperature had a marked effect on P release to solution with the maximum P release to solution occurring at the higher temperature level. Algal growth on standard media containing only P released from the sediments was equivalent to orthophosphate-P.

Direct equilibration of the sediments with anion exchange resin markedly increased P release relative to sediments not containing resin. The presence of a P sink therefore had a substantial influence on the quantity of P released to solution indicating that under the proper circumstances biological growth might function in an analogous manner. Approximately 33% of total sediment P was released to the resin from the sediment which exhibited maximum changes in the field compared to < 15% for other lake locations which varied less on a seasonal basis. This relatively simple equilibration method resulted in the release of considerably more P from the sediments than other methods and the quantity released approximated maximum seasonal variation for the sediments studied. This technique therefore would appear amenable to measurement of the potential for maximum P release to solution and useful in evaluating the influence of this parameter for comprehensive lake management.

SECTION II

RECOMMENDATIONS

This program was limited primarily to basic studies of the chemical nature of lake sediment P and the potential for P release from sediments. Although development of remedial measures for stabilization of sediment P was not within the scope of this program, the background information on Upper Klamath Lake sediments presented here may be used in evaluation of the necessity and general types of control measures. In addition, the experimental techniques and procedures that were established should prove useful in future evaluation of lake systems.

In lake management, the sediments must be viewed in the perspective of the total lake system. The potential for release of P from sediments may or may not be significant relative to other factors influencing eutrophic process in a particular lake system. An indication of this significance may be obtained by using lake nutrient budgets in which the distribution of P in the various ecological compartments is determined. The inorganic P is the most labile fraction. If the inorganic P in sediments, assuming that it was all released, is of sufficient magnitude to influence remedial procedures, the potential for P release and its effects should be considered.

It is likely that measures can be developed which limit P input into a particular lake system. The principal problem thus becomes that of estimating the potential P release from sediments over the long term. With this knowledge, decisions can be made as to the efficacy of treatment of input waters and, subsequently, treatment of sediments as necessary. To obtain this information it is necessary to have enough samples to satisfy statistical criteria, estimate potential P release under conditions optimum for release and estimate the potential for increased biological growth resulting from release. This information can then be used in conjunction with a nutrient budget to establish the necessity for treatment.

The results of these investigations indicate that sediments within a lake system are not necessarily uniform with respect to P composition or ability to release P. Therefore, a suitable sampling scheme must be devised. This may be accomplished as described in the Appendix of this report. In general, analyses of sediments taken from lake transects may be categorized as to P concentration and permanent sample sites, identified using a

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grid system, randomly selected from these categories. Evidence presented in this report indicates that seasonal sampling at these sites may be warranted to accurately bracket sediment P concentrations.

Several relatively simple methods were devised to estimate the potential for P release from sediments. The sediment-anion exchange resin equilibration method gave maximum release. These data should be evaluated for individual lake systems in terms of the potential influence on P concentration of lake waters and on biological growth over the long term. Long-term effects should be considered because orthophosphate concentration of lake waters may remain quite low yet support algal growth. The present investigations indicate that for practical purposes P released may be considered to have the algal growth potential of orthophosphate P.

In the case of Upper Klamath Lake sediments, chemical treatments which will minimize release of non-occluded Fe-P should be initially evaluated. These may include treatments which result in maximal sediment pH and aeration, minimizing Fe-P solubility. Since Al-P appears to be largely responsible for sorption of P, a treatment which also increased the concentrations of sediment Al would appear desirable. Colloidal slurries of Al hydroxide or silicate may serve multiple purposes in this regard. The dialysis system utilized in these investigations may find unique application in testing potential remedial procedures. The lake water may be individually treated and the influence on P release from the sediments evaluated.

SECTION III

INTRODUCTION

Eutrophication, the process of water enrichment, is of considerable national concern. Increases in the quantities of nutrients disposed to the nation's waters by municipal, industrial and agricultural activities have been accompanied by an increase in the requirements of a growing population for water of high quality. Thus, although eutrophication is a natural process normally accompanying lake aging, dramatic changes in national priorities and needs require that direct action be taken to reverse the eutrophic process in many waters.

One of the most important results of eutrophication is the development of undesirable biological populations. The normal N concentrations of most lakes are sufficient to support the vigorous biological growth observed in eutrophic lakes, but it is likely that the small quantities of naturally available P are not. Thus, although the relative importance of nutrients required for phytoplankton growth is a subject of recent controversy, the supply of P to the lake and P availability to the biota may be prime factors controlling the rate and extent of eutrophication.

The sources of P to waters are varied and include industrial and municipal wastes, surface runoff, and return from irrigation and ground water. Reactions which may deplete the supply of P in fresh waters are equally complex and include uptake by the aquatic biota, precipitation, and sorption by suspended particles and bottom sediments. These depletion reactions may be in part reversible, thus functioning as future sources of P to the lake.

The possibility that bottom sediments may function as a reservoir of available nutrients to eutrophic lake waters has long been acknowledged but, at the onset of the program, little definitive information on the rate and extent of P release and the factors influencing release was available. This information is essential because sediments may have the capacity to resupply nutrients removed from lake water, or streams influent into lake water, by newly developed chemical treatment processes.

The exchange of P between sediments and the overlying water appears to be dependent upon a number of chemical, physical and biological parameters as summarized by Lee (1970). Laboratory studies (Gerhold and Thompson 1969; Golterman et al. 1969) have shown that sediments may serve as a sole source of P to algae which function as a biological sink for P in water resulting in the dissolution of phosphate minerals.

In order to provide insight into the effects of environmental factors on the rate of P release to solution and subsequent availability to algae, a study was designed to determine (*i*) the predominant inorganic and organic forms of P in sediments of the Upper Klamath Lake, Oregon, (*ii*) the rate of release of soluble P from the solid phase with changes in environmental parameters of temperature, pH, and water and sediment composition and (*iii*) the relationship of P release to algal growth requirements.

Initially the program was conceived as primarily a laboratory study. However because of the concurrent EPA program dealing with the water quality of Upper Klamath Lake, the principal portion of the research effort during the first two years (1969, 1970) of the program was designed to determine if detectable quantities of P were released from sediments. This release was detected by monitoring changes in the concentration of total sediment P, inorganic P and organic P on a seasonal basis and correlating these changes with limnological changes which may have affected the release of P. Inherent in these studies was the development of statistically suitable methods for lake sediment sampling and methods for the characterization and measurement of sediment P components. Subsequently, laboratory methods were developed for measurement of P release to solution and P availability to algae. In all investigations emphasis was placed on identification of the labile forms of sediment P and upon estimation of the maximim potential for P release. Thus, a background of information was provided to evaluate the necessity for specific chemical control measures designed to stabilize labile sediment P forms.

With the development of satisfactory methods for sediment P determination, these methods were applied to the characterization of sediments from Shagawa Lake, Minnesota; Agency Lake, Oregon; Diamond Lake, Oregon and Lake Erie to provide a basis for future EPA nutrient modeling efforts. The extension of research to these lake systems allowed broader development and testing of statistical methods for sediment sampling and chemical methods of P measurement. These data are included in the Appendix section of this report. However, Upper Klamath Lake received principal research emphasis particularly in terms of determination of the factors influencing P release, and it is this lake system which will be discussed in detail in the text of this report.

SECTION IV

PHOSPHORUS STATUS OF LAKE SEDIMENTS AS RELATED TO CHANGES IN LIMNOLOGICAL CONDITIONS

Because little was known of the forms of P present in lake sediments or of the availability of sediment P to biota in the overlying waters, an initial study was undertaken to develop methods for measurement of total sediment P and for characterization of sediment P mineral and organic components. These methods were subsequently applied to sediments from Upper Klamath Lake sampled on a seasonal basis to determine (*i*) if detectable quantities of P were released or taken up by sediments, (*ii*) the fraction of sediment P responsible for release or uptake and (*iii*) environmental parameters influencing sediment P transformations. Total, inorganic and organic sediment P were monitored over a two-year period. These results are summarized in Part A of this section.

Sediments exhibiting marked changes in P with changes in limnological conditions were analyzed in more detail to determine the most labile P mineral or organic P components. Identification of components most responsive to changes in limnological conditions may allow the development of specific chemical treatments to stabilize sediment P. These results are summarized in Part B of this section.

A. TOTAL, INORGANIC AND ORGANIC PHOSPHORUS

This study was designed to (*i*) evaluate several techniques used for characterizing sediment P, (*ii*) determine if seasonal changes in composition of lake sediments necessitated seasonal sampling to obtain representative data, (*iii*) determine if detectable quantities of P were released from sediments by monitoring changes in the concentration of total sediment P, inorganic P and organic P on a seasonal basis and (*iv*) correlate these changes with limnological changes which may have affected the release of P.

Methods and Materials

Sediment Sampling and Characterization

Sediment samples were taken to an approximate depth of 10 cm with an Ekman dredge from three locations on Upper Klamath Lake in south-central Oregon (Figure 1) during the 1969 and 1970 seasons. The sampling locations were selected on the bases

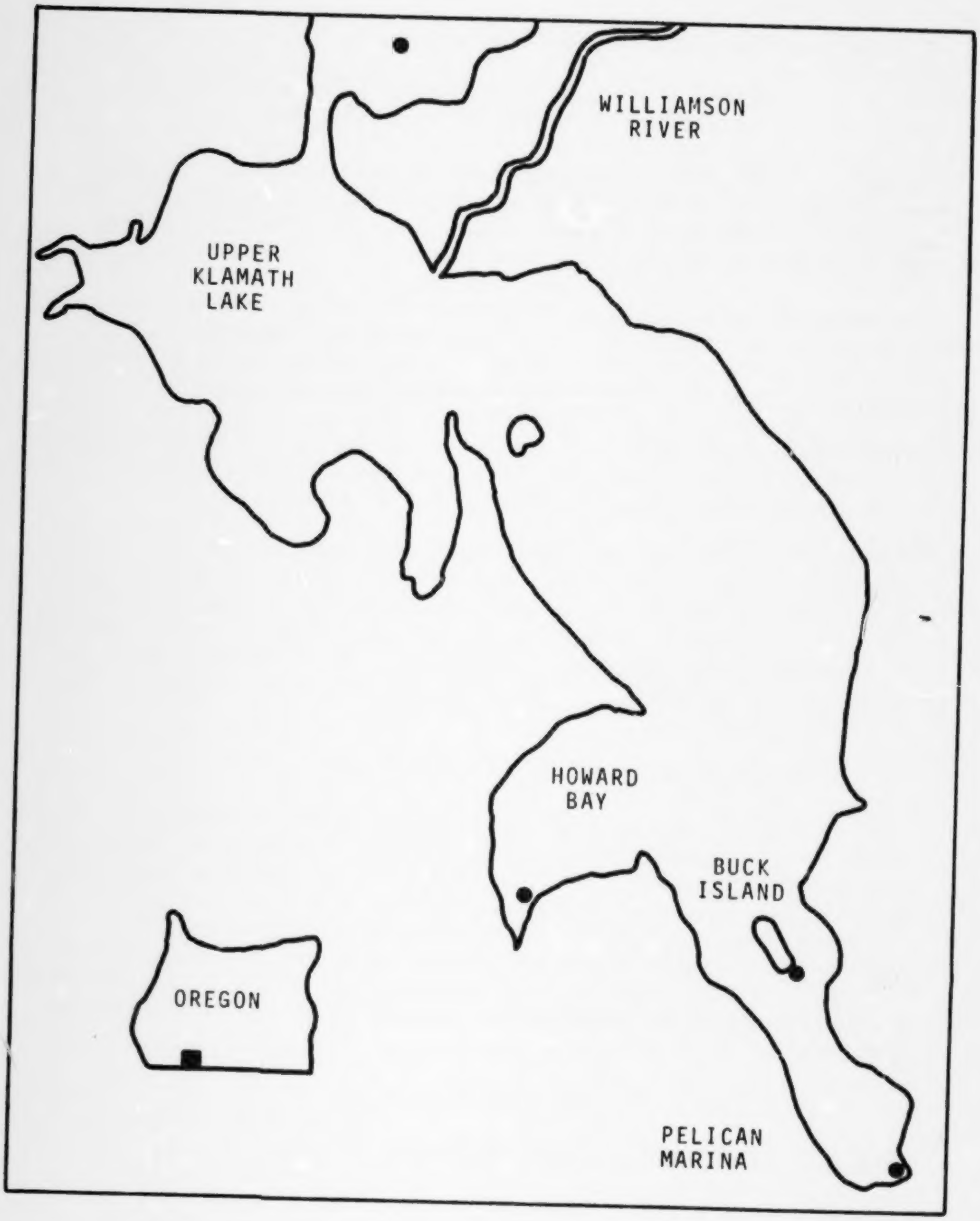
WILLIAMSON RIVER
UPPER KLAMATH LAKE
HOWARD BAY
BUCK ISLAND
OREGON
PELICAN MARINA

FIGURE 1. LOCATION OF SAMPLING SITES ON UPPER KLAMATH LAKE, OREGON.

of representative locations and water depth. The sediments from sites designated Howard Bay, Buck Island and Pelican Marina were sampled at approximately monthly intervals during the period of maximum lake biological activity (May to September); fall and winter samplings were less frequent (Table 1). The samples were packed and transported in ice and then placed under refrigeration at 4 C in the laboratory. Subsamples of the moist sediments were analyzed directly after remixing and drying at 60 C for 48 hours.

The sediments were initially characterized as to mineral composition (Whittig, 1965) and cation exchange capacity (Hajek and Wildung, 1969). Sediment total solids, pH and carbonate content were routinely measured on each sample.

Sediment organic C and N monitored during the 1969 season were determined, respectively, by microcombustion techniques (Hajek and Wildung, 1969) and by the Dumas method (Welcher, 1966).

To determine variability associated with sediment sampling at the selected sites a total of 8-10 sediment samples, representing 2-3 dredge loadings per sample, were taken at each site in April, 1970 and subsampled in duplicate for analyses of total and inorganic P.

Water Analyses

The Environmental Protection Agency maintained a concommitant program of lake water analyses during 1969. Parameters measured in lake water pertinent to the present studies included total N, NH_3-N, NO_3-N, total and organic C, turbidity (Secchi disc), pH and temperature (Gahler, 1969).

Phosphorus Analyses

Preliminary investigations were conducted to determine the applicability of several analytical techniques for total P and inorganic P to lake sediment systems. These investigations were continued during the course of the study to include sediment samples differing in chemical characteristics with time. Means of P values determined by each method were compared for 5 sediment samples from each of 3 lake locations (n = 15). For these purposes, total P in the sediments was determined by Na_2CO_3 fusion (Jackson, 1958), high temperature ignition (Walker and Adams, 1958) and extraction (Mehta et al., 1954) techniques. Inorganic P solubilized by these methods was analyzed

Table 1. Description of sampling sites on Upper Klamath Lake, Oregon.

Sample designation	Date of collection	Location
H-1	5-7-69	42° 18.5'N, 121° 50.7'W (Howard Bay)
H-2	6-3-69	
H-3	7-15-69	
H-4	8-28-69	
H-5	10-21-69	
H-6	1-13-70	
H-7	3-25-70	
H-8	4-27-70	
H-9	6-3-70	
H-10	7-7-70	
H-11	8-11-70	
H-12	9-17-70	
H-13	4-13-71	
B-1	5-7-69	42° 17.5'N, 121° 50.7'W (Buck Island)
B-2	6-3-69	
B-3	7-15-69	
B-4	8-28-69	
B-5	10-21-69	
B-6	2-24-70	
B-7	3-25-70	
B-8	4-27-70	
B-9	6-3-70	
B-10	7-7-70	
B-11	8-11-70	
B-12	9-17-70	
B-13	4-13-71	

Table 1. (Cont.)

Sample designation	Date of collection	Location
P-1	5-7-69	42° 14.3'N, 121° 48.5'W (Pelican Marina)
P-2	6-3-69	
P-3	7-15-69	
P-4	8-28-69	
P-5	10-21-69	
P-6	1-13-70	
P-7	2-24-70	
P-8	3-25-70	
P-9	4-27-70	
P-10	6-3-70	
P-11	7-7-70	
P-12	8-11-70	
P-13	9-17-70	
P-14	12-10-70	
P-15	4-13-71	

by the method of Fogg and Wilkinson (1958).

Sediment inorganic P concentrations were estimated by H_2SO_4 extraction (Walker and Adams, 1958), and by summation of non-occluded inorganic P fractions (Williams, et al., 1967).

Routine measurements of total P and inorganic P reported herein were conducted using the high temperature ignition and H_2SO_4 extraction methods, respectively (Walker and Adams, 1958). Organic P was taken as the difference between total and inorganic P.

Results and Discussion

Upper Klamath Lake has a surface area of 31,000 ha and a mean depth of 2.5 m. It does not receive municipal sewage, and nutrients in drainage from cultural activities are estimated (Miller and Tash, 1967) to account for less than 25% of the total nutrient input into the lake system. However, the lake is eutrophic, apparently as a result of natural aging processes. A nuisance bloom of blue-green algae, primarily *Aphanizomenon flos-aque* has occurred for many years. The time and species distribution of nuisance blooms vary from year to year, but follow a general pattern of a spring bloom of diatoms and an early summer bloom of blue-green algae.

The sediments of Upper Klamath Lake are neutral to slightly acidic, noncalcareous and silty clay in texture (Table 2). Major clay mineral components are chlorite, vermiculite and mica. The cation-exchange capacity of the sediments ranged from 33 to 55 me/100g with differences likely resulting from differences in clay content. The C, N and P contents of the Howard Bay and Pelican Marina sediments varied significantly with season and will be separately discussed in a following section.

Estimation of Sampling and Analytical Variability

The combined effects of sampling and analytical variability of P at the selected sampling sites are outlined in Table 3. The standard deviations (n = 8-10) for this sampling interval were taken as indicative of sampling and analytical variation throughout the season. Variations in total and inorganic P of replicate samples taken throughout the year approximated those obtained in this study. Sediment P values which differed by more than one standard deviation were therefore taken as real differences.

Table 2. Depth and chemical properties of sediments, Upper Klamath Lake, Oregon.

Sample Location	Overlying water depth	pH	CO_3-C ($CaCO_3$ equivalent)	Cation exchange capacity	Major clay mineral components
	m		mg/g	me./100g	
Howard Bay	2.5	6.4-6.9	<0.5	33	
Buck Island	2.7	6.2-6.9	<0.5	36	chlorite vermiculite mica
Pelican Marina	3.4	6.1-7.3	<0.5	55	

Table 3. Sampling and analytical variability associated with the determination of total and inorganic phosphorus in lake sediments.

Total P			Inorganic P		
Mean	Standard Deviation	Coefficient of Variation	Mean	Standard Deviation	Coefficient of Variation
μg/g		%	μg/g		%
			Howard Bay		
1033	48.1	4.7	574	52.7	9.2
			Buck Island		
629	26.7	4.3	295	28.7	9.8
			Pelican Marina		
662	17.5	2.6	348	11.9	3.4

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[1] Based on oven dry (60 C) weight.

[2] Means of 8-10 samples analyzed in duplicate at each location.

Evaluation of Methods for P Analyses

Preliminary studies in Upper Klamath Lake sediment systems indicated a relatively close agreement between the Na_2CO_3 fusion and the HCl-NaOH extraction methods for total P (Figure 2). The ignition method resulted in significantly lower P values than either the fusion or extraction methods [p (probability) < 0.01]. The ignition method consistently gave results for total P that were about 8% lower than results from Na_2CO_3 fusion or extraction methods. A similar phenomenon was observed in ancillary studies with lakes from other regions.

Estimates of total P obtained by summing (*i*) the quantity of residual occluded P solubilized by Na_2CO_3 fusion after serial extraction of inorganic P (Williams et al., 1967) with (*ii*) the total P measured by high temperature ignition were not significantly different than total sediment P as measured by Na_2CO_3 fusion methods (Figure 2). This suggests that a portion of the inorganic P was present in mineral occluded forms which were not subject to extraction after ignition. However, the possibility that organic P was volatilized during ignition would also account for the observed low total P values using the ignition method. To investigate this possibility, sediment samples were ignited and the ash remaining after ignition subjected to Na_2CO_3 fusion. Ignition prior to fusion did not reduce measured total P content relative to Na_2CO_3 fusion only. Apparently no P was lost through volatilization on ignition, and low recovery by the ignition method may have resulted from the lack of H_2SO_4 extractability of naturally occluded minerals or the effect of ignition on the extractability of sediment P as suggested by Sommers et al., (1970). These investigations were concerned with comparative changes in lake sediments and differences between the Na_2CO_3 fusion and ignition methods were relatively small and consistent. The simpler ignition method was therefore used for routine analyses of total P.

Estimates of inorganic P in sediment samples from all locations throughout the 1969 season by (*i*) H_2SO_4 extraction (Walker and Adams, 1958) and inorganic P fractions (Williams et al., 1967) were not significantly different ($p < 0.05$). It was therefore concluded that for routine measurements of inorganic P potentially available to solution in these systems the simpler H_2SO_4 extraction was the method of choice.

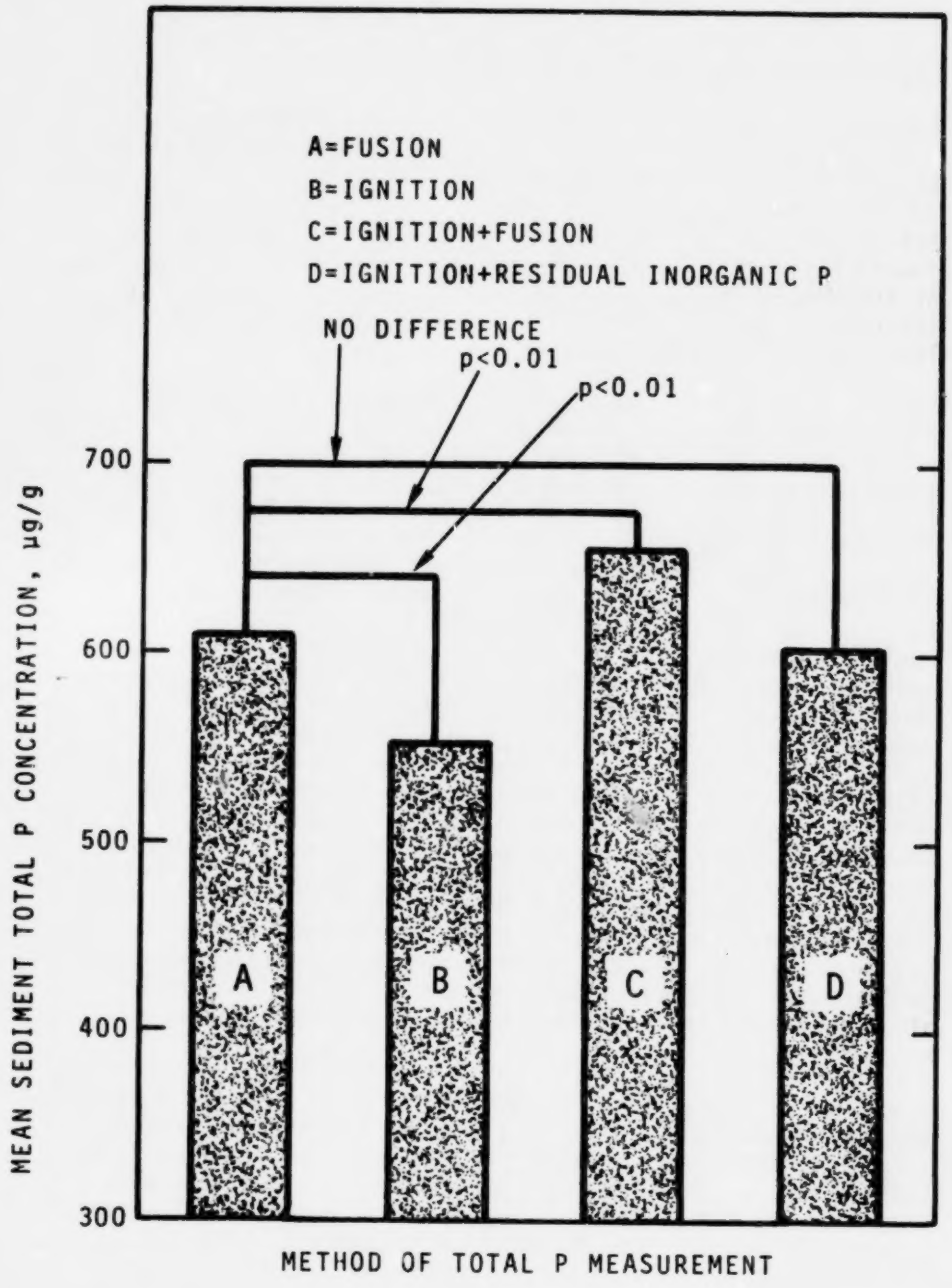


FIGURE 2. COMPARISON OF METHODS FOR DETERMINATION OF TOTAL SEDIMENT PHOSPHORUS CONTENTS.

Seasonal Changes in Sediment Composition

Seasonal changes in total, inorganic and organic sediment P concentrations at the three sampling locations on Upper Klamath Lake during 1969 and 1970 are summarized in Figure 3. Total P ranged from 413 to 1070 μg/g for Buck Island, 521 to 629 μg/g for Pelican Marina and 437 to 707 μg/g for Howard Bay. Thus, the greatest variability in total P occurred at the Howard Bay location with less pronounced changes at the Pelican Marina location. Sediments at the Buck Island location did not exhibit large seasonal variations.

Total sediment P at the Howard Bay location decreased markedly from May to June and July, 1969. By August, the total P content of the Howard Bay sediment had increased to levels above those observed earlier and August levels were apparently maintained through March, 1970. In April, 1970, a marked reduction in total P to the low levels observed in 1969 occurred. Analyses during the remainder of the summer of 1970 indicated a return of total P to previous high levels followed by a depression in P content in August and an increase to 1070 μg/g in September. Total P in April, 1971 (not shown) was 1033 μg/g indicating an overall increase in sediment P from the spring of 1969 to the spring of 1971. In contrast to the other locations, Howard Bay annually receives land runoff waters as a result of fall flooding of adjacent agricultural lands for rodent control. The lands are drained into the bay in the spring prior to planting. Total P in sediments of Pelican Marina reached a minimum in July, 1969 and increased to a maximum in January, 1970, with an overall increase in total P between June, 1969 and April, 1971 amounting to 110 μg/g.

Changes in inorganic sediment P (Figure 4) were closely correlated [r (correlation coefficient) = 0.960] to total sediment P at all locations. If it is assumed that total and inorganic P are statistically independent and have equal variances, the r value for total and inorganic P may be expected to approximate 0.707. On this basis it is possible to test the significance of r (Snedecor, 1956). The r value for total and inorganic P is significant ($p < 0.01$) indicating the inorganic P fraction was responsive to changes in lake conditions which affected total sediment P content. In fact, changes in inorganic P accounted for a major portion of the changes in total sediment P. In the case of the sediments exhibiting the most marked change in total P, (Howard Bay from May to June 1969) inorganic P accounted for 80% of the reduction in total P.

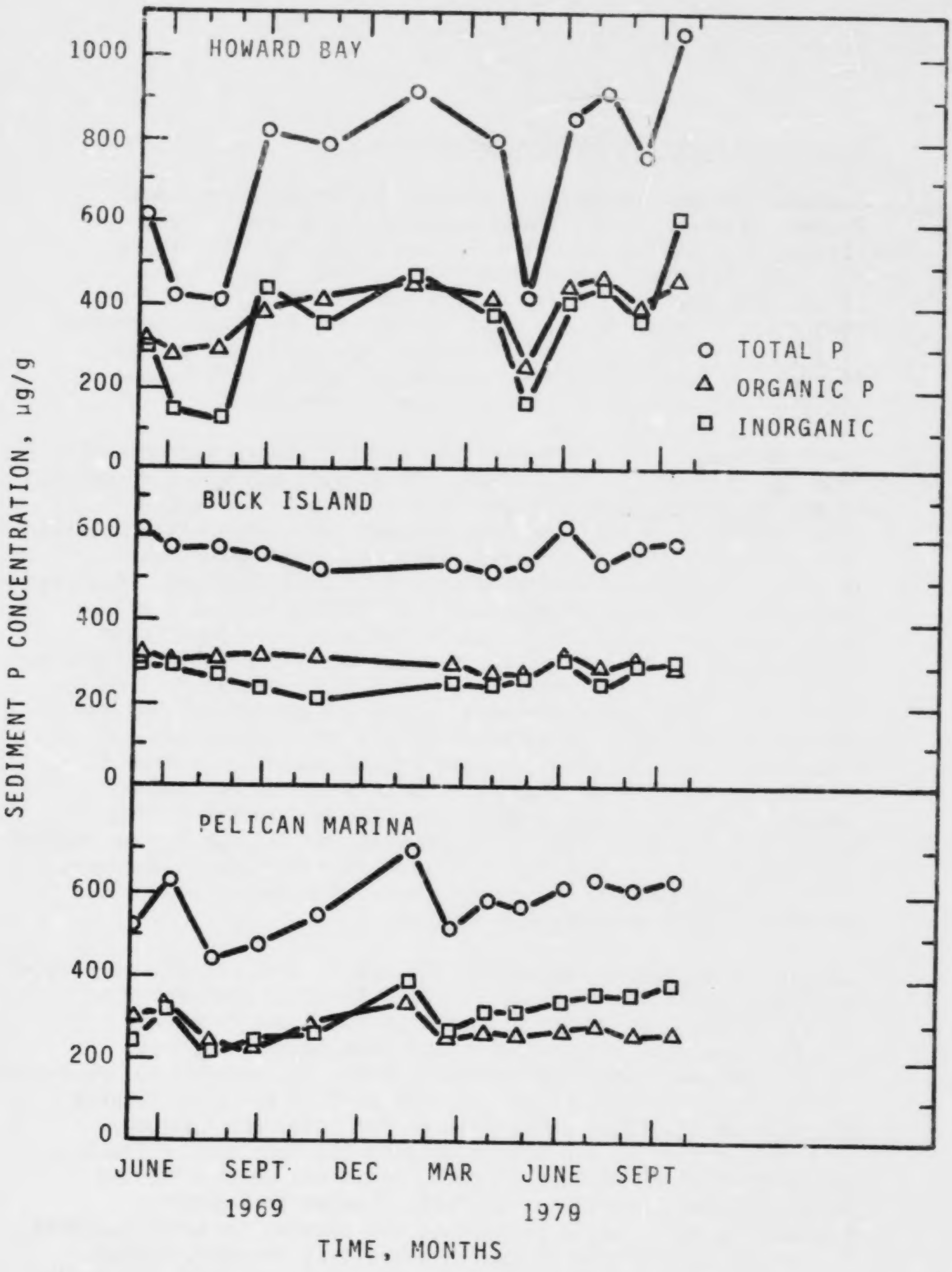
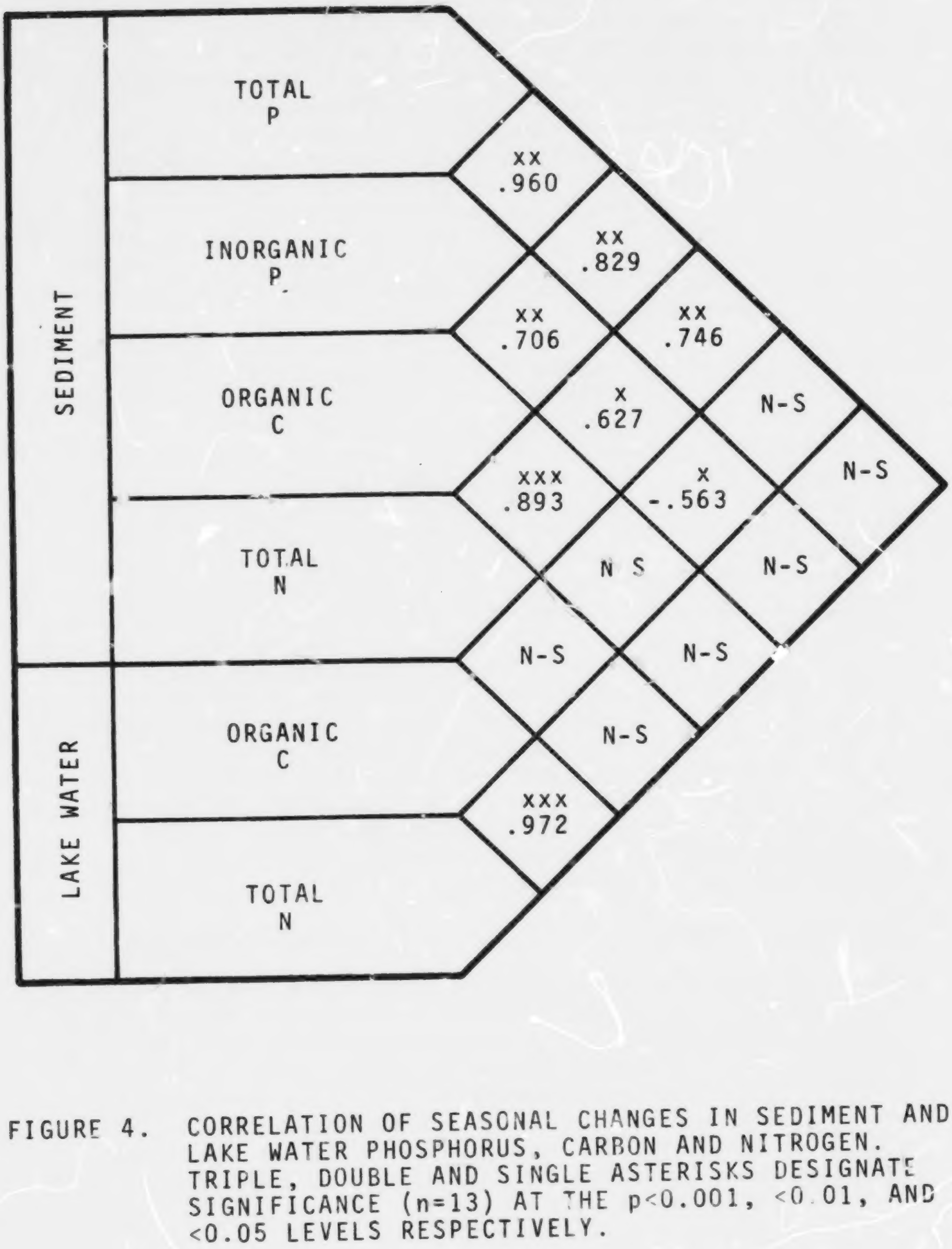


FIGURE 3. SEASONAL CHANGES IN TOTAL, INORGANIC AND ORGANIC SEDIMENT PHOSPHORUS CONCENTRATIONS AT THREE SAMPLING LOCATIONS ON UPPER KLAMATH LAKE.



		TOTAL P	INORGANIC P	ORGANIC C	TOTAL N	ORGANIC C
SEDIMENT	INORGANIC P	xx .960				
SEDIMENT	ORGANIC C	xx .829	xx .706			
SEDIMENT	TOTAL N	xx .746	x .627	xxx .893		
LAKE WATER	ORGANIC C	N-S	x -.563	N-S	N-S	
LAKE WATER	TOTAL N	N-S	N-S	N-S	N-S	xxx .972

FIGURE 4. CORRELATION OF SEASONAL CHANGES IN SEDIMENT AND LAKE WATER PHOSPHORUS, CARBON AND NITROGEN. TRIPLE, DOUBLE AND SINGLE ASTERISKS DESIGNATE SIGNIFICANCE (n=13) AT THE $p<0.001$, <0.01, AND <0.05 LEVELS RESPECTIVELY.

Although changes in inorganic P appeared to account for most of the changes in total P, changes in sediment organic C during the 1969 season (Table 4) closely paralleled changes in total P (Figure 3) at Howard Bay and Pelican Marina sites with little change occurring at the Buck Island location. Combining data from all locations, sediment organic C was correlated ($r = 0.829$; $p < 0.001$) to total P during the 1969 season. Changes in organic C were most pronounced at the Howard Bay location. A fraction of sediment organic C was apparently mineralized during the spring, decreasing at Howard Bay from May to June, 1969 (Table 4). A portion of this organic material was evidently organic P, changes in which were significantly related ($r = 0.880$; $p < 0.05$) to changes in organic C for the Howard Bay sediments. Organic C increased from July to October 1969, likely due to the deposition of plankton detritus.

The C:N ratio of the sediments at all locations was quite constant throughout the season ranging from 6.1 to 7.1 (Table 4). Utilizing combined data from all sample sites during the 1969 season, changes in total sediment N were correlated to organic C ($r = 0.893$; $p < 0.001$) and to total P ($r = 0.716$; $p < 0.001$). The correlation of total N to organic C for all sample sites was due primarily to the close relationship between seasonal changes in sediment concentrations of these elements at the Howard Bay and Pelican Marina sites. Reductions in the concentrations of sediment C during the spring and early summer at Howard Bay were accompanied by proportionate reductions in sediment N as might be expected if sediment biota were active in the mineralization of C. Increases in sediment N occurred during the late summer and fall, apparently resulting, analagous to C, from the deposition of plankton detritus. The C:N ratio of the sediments was higher than might be expected if they consisted solely of fresh phytoplankton tissue (C:N ratio approximately 5:1). A portion of the N in the tissue must therefore have been mineralized during settling or on deposition in the sediments.

Influence of Limnological Conditions on Sediment Composition

Biological Activity. Decreases in total P and inorganic P in Howard Bay sediments in the early summer of 1969 (Figure 3) corresponded to the period of exponential growth of Aphanizomenon flos-aque, the predominant blue-green algae in the lake system. Secchi disc measurements in Howard Bay during June and July, 1969 were 34 and 10 cm, respectively, compared with 70 cm or greater during August and September indicating increased wat r turbidity and algal growth during the early summer.

Table 4. Seasonal changes in sediment organic carbon and total nitrogen.

Sampling date*	Sediment concentration of Carbon	Sediment concentration of Nitrogen	Ratio of Carbon/Nitrogen
	-------------	%-------------	
	Howard Bay		
5-7	7.9	1.12	7.1
6-3	6.4	0.98	6.5
7-15	6.6	0.94	7.0
8-28	7.7	1.09	7.1
10-21	8.6	1.28	6.7
	Buck Island		
5-7	6.9	1.06	6.5
6-3	6.8	1.12	6.1
7-15	6.5	1.02	6.4
8-28	6.3	0.92	6.9
10-21	6.7	0.95	7.1
	Pelican Marina		
5-7	6.3	0.91	6.9
6-3	6.9	1.00	6.9
7-15	6.3	0.95	6.6
8-28	6.4	0.93	6.8
10-21	6.8	0.97	7.0

*1969

In June and July, Secchi disc readings at other lake locations were in excess of 70 cm suggesting less phytoplankton growth at these sites relative to Howard Bay. An *Aphanizomenon* bloom of similar magnitude occurred at the same time in 1968, but measurements of sediment nutrient levels were not initiated until 1969. The *Aphanizomenon* bloom in 1970 was not of the same magnitude as observed in 1969 with Secchi disc measurements at the Howard Bay location in June and July, 1970 of 140 and 200 cm, respectively. Reductions in sediment P (Figure 3) in April, 1970 and August, 1970 coincided with an extensive increase in diatom numbers in April and a delayed *Aphanizomenon* bloom in August. Considerable quantities of sediment P were thus released at times of maximum biological growth in Howard Bay. These losses from the sediments were not reflected in increased concentrations of P in the waters.

Phytoplankton use of P in Howard Bay evidently provided a substantial biological sink that reduces the solution concentration of orthophosphate and decreases total sediment P. Concurrently, N and organic C were also released from the sediment. These effects were not as pronounced at the other sample locations perhaps due to relatively less phytoplankton growth in waters at these locations as exhibited by lower turbidities during this period. Sediment interstitial water concentrations of orthophosphate at Howard Bay in April 1969 were higher (7.1 mg/liter) than other lake locations (< 0.5 mg/liter) perhaps as a result of agricultural runoff to the bay in the early spring. This additional P, if available to the biota, may have provided the impetus for the increased growth which results in sediment P release in the early summer. Increases in total P, organic C and N from August to January, 1969 apparently resulted from the deposition on the sediment and partial mineralization of large quantities of dead algal tissue as the algal population declined.

Surface Water Parameters. An examination of the chemical composition of the lake water (Table 5) during the 1969 season provides further insight into the lake phenomena influencing sediment P, C and N status. During this period the concentration of soluble orthophosphate in the water of Howard Bay remained at < 0.01 mg/liter. However, organic C contents, a measure of biological activity, increased from 4 mg/liter in May to 10 and 23 mg/liter in June and July and then decreased to 7 mg/liter in August. Organic C contents of lake waters from the other sampling locations did not exceed 9 mg/liter over the same period. Organic C in the lake waters was negatively correlated ($r = -0.563$; $p < 0.05$) with sediment inorganic P when data from all locations was combined. This is further

Table 5. Seasonal changes in elemental composition, pH and temperature of surface waters.

Sampling* date	Nitrogen			Carbon		Orthophosphate	pH	Temperature
	total	ammonium	nitrate	total	organic			
	mg/liter						units	°C
				Howard Bay				
5-7	0.8	0.05	<0.01	14	4	<0.01	7.0	13.2
6-3	5.3	2.70	0.01	35	10	<0.01	9.5	19.0
7-15	14.6	11.00	0.09	35	23	<0.01	8.4	19.2
8-28	3.3	1.30	0.04	25	7	<0.01	9.4	18.3
10-21	3.2	0.70	<0.01	25	7	<0.01	8.3	8.5
				Buck Island				
5-7	0.8	0.06	<0.01	14	4	<0.01	8.5	13.5
6-3	1.4	0.47	<0.01	18	5	<0.01	9.2	18.5
7-15	2.0	0.08	<0.01	19	9	<0.01	9.4	19.0
8-28	2.3	0.40	<0.01	22	7	<0.01	9.7	17.6
10-21	2.6	0.07	<0.01	22	7	<0.01	8.8	8.5
				Pelican Marina				
5-7	0.6	0.03	<0.01	14	4	<0.01	6.4	13.4
6-3	1.6	0.52	<0.01	21	4	<0.01	9.6	18.3
7-15	2.8	0.23	<0.01	22	7	<0.01	9.6	18.5
8-28	2.9	0.72	<0.01	22	6	<0.01	9.7	18.9
10-21	3.8	0.04	<0.01	22	6	<0.01	8.3	8.5

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*1969 season

evidence that the lake sediments served as reservoir of inorganic P to support biological growth in the lake waters.

Paralleling organic C, the marked increases in total N, NH_3-N and NO_3-N (Table 5) that occurred in the waters of Howard Bay during the early summer reflect increased production of biological tissue and increased biological activity. A decrease in N forms occurred from July to August. Thus the C and N analyses tend to substantiate turbidity measurements and visual observations of heavy phytoplankton growth in Howard Bay relative to the other locations in June and July. At the Buck Island and Pelican Marina locations, total N in water increased gradually from May to October (Table 5). Combining water data from all lake locations, total N was highly correlated to organic C ($r = 0.972$; $p < 0.001$). As in the case of Howard Bay, the NH_3-H contents at Buck Island and Pelican Marina were highest during the late spring and summer months with minimum levels occurring in May and October. However, the magnitudes of the changes were much less than for the Howard Bay location. In contrast to the waters of Howard Bay, NO_3-N did not exceed 0.01 mg/liter throughout the season.

At all lake locations surface water pH (Table 5) was higher during the summer than the spring and fall reflecting increased biological utilization of CO_2 during the summer. The water pH was not, however, significantly correlated to changes in sediment P, N or C.

Water temperature (May, 1969 to January, 1970) was negatively correlated ($r = -0.755$; $p < 0.05$) to total sediment P in Howard Bay sediments (Figure 3, Table 5). That is, sediment P concentrations tended to decrease with increased temperature and increase with decreased temperature. Changes in water temperatures were approximately equivalent at other locations but these changes were not related to release of P from the sediment. Thus, temperature alone cannot explain the variations in sediment total P observed at the Howard Bay location but rather appeared to play an indirect role in influencing biological growth.

B. PHOSPHORUS MINERAL AND ORGANIC COMPONENTS

The concentrations of total P in the sediments of Western Lake Erie have been recently shown (Skoch, 1968) to change greatly on a seasonal basis and the changes appear to be related to changes in total Fe and C. In concurrent investigations (Section IV, A) dealing with the relationship of sediment P to water quality in Upper Klamath Lake, significant seasonal changes in total sediment P were also observed. In the Upper Klamath Lake studies, variations in total sediment P were correlated with changes in sediment inorganic P and with organic C. Inorganic P appeared to account for a major portion of the variation in total sediment P. These effects were particularly pronounced at the Howard Bay location where sediments exhibited a marked reduction in total P and inorganic P during the early summer, evidently releasing P in response to the utilization of orthophosphate by a heavy bloom of blue-green algae. Increases in sediment P and organic C followed cessation of the algal bloom apparently as a result of the deposition of algal detritus. Thus, in addition to a planned examination of the changes in sediment P mineral components on a seasonal basis we had an opportunity to investigate the chemical changes in the sediment inorganic and organic P fractions when occurred in the field in response to biological demands and upon deposition of organic detritus following the cessation of phytoplankton growth in the late summer and fall.

This investigation was designed to determine (*i*) the relative changes in concentration of chemically defined P mineral fractions responsible for seasonal changes in sediment inorganic P and (*ii*) the distribution of C and P in the benzene-ethanol soluble, humate and fulvate components of the sediment organic fraction during phytoplankton growth and upon deposition of phytoplankton detritus.

Materials and Methods

Sediments were sampled periodically during the 1969 and 1970 seasons from three locations (Howard Bay, Buck Island and Pelican Marina) on Upper Klamath Lake as previously described. Sediments exhibiting marked seasonal changes in P distribution in inorganic and organic P fractions during the first year were further examined to determine if observed changes in total P status could be attributed to specific inorganic and organic chemical fractions.

Phosphorus Mineral Components

Total P was determined by Na_2CO_3 fusion (Jackson, 1958). The inorganic P fraction of sediments sampled from all locations during May, June, July, August and October, 1969 were characterized using the serial extraction techniques (Table 6) of Chang and Jackson (1957) as modified by Williams, et al. (1967). The method was further modified (Results and Discussion Section) to obtain complete recovery of added P in the reductant-soluble

P fraction. Inorganic P was estimated by H_2SO_4 extraction (Walker and Adams, 1958) and summation of non-occluded inorganic P fractions 1-6 (Table 6). Inorganic P values obtained by these methods were not significantly different for these sediments (Section IV, A).

Organic Phosphorus Components

To provide insight into the chemical changes which may have occurred concommitantly with changes in sediment concentrations of total P and C, the sediments of Howard Bay, sampled in May, June, July and August (Table 1), were fractionated into benzene-ethanol (1:1) soluble, NaOH soluble-HCl insoluble (designated humic acid), and NaOH-HCl soluble (designated fulvic acid) components as described by Wildung et al. (1965, 1971). The yields of organic matter, total P and organic C were measured for each extract. The fulvic acid components were further characterized as described for soil systems by Forsyth (1947) and Stevenson (1965a) by concentration from aqueous solution on activated C and serial dissolution of the adsorbed material with acetone (90%), distilled H_2O and NaOH (0.5 M), yielding the fractions described in Table 7.

Techniques were developed to measure sediment levels of inositol hexaphosphate, believed to constitute the bulk of the organic phosphorus in soils. The method described by Caldwell and Black (1958) and Stevenson (1965) for isolation of inositol hexaphosphate from soils was initially evaluated for application to sediment systems. In general, the method involved successive extractions of soils with HCl (concentrated) and NaOH (0.5 N) to remove separate inositol hexaphosphates.

Organic contaminants were removed from the NaOH extract by precipitation at pH 1.0 or less and centrifugation. The HCl and purified NaOH extracts were combined and the Fe salt of inositol hexaphosphate was precipitated by titration (NaOH) to pH 1.8. The precipitate was dissolved in 0.85 N HCl and the solution eluted through a glass column containing an anion exchange resin. The inositol hexaphosphate and lower phosphate esters of inositol and inorganic P were removed by elution with increased concentrations of acid. Direct application of the method published for soils resulted in incomplete recoveries of inostiol hexaphosphate from sediments and therefore several modifications were employed as outlined in the Results and Discussion Section.

Table 6. Serial extraction procedure employed for the fractionation of sediment inorganic phosphorus[1].

Treatment Number	Treatment	Time	Probable major mineral P extractives
		hr	
1	NH_4Cl (0.5M)	0.5	Readily soluble P
2	NH_4F (0.5M, pH 8.2)	24	Al-P
3	NaOH (0.1M)	17	Fe-P
4	$Na_2S_2O_4$ (0.1M) $Na_3C_6H_5O_2 \cdot 2H_2O$ (0.3M, pH 7.3)	0.3	Fe, Al-oxide occluded Fe-P, Al-P
5	NaOH (1.0M)	17	Fe, Al-oxide occluded (Al, Fe)-P
6	HCl (0.5M),(1.0M)	1,5	Ca-P
7	Ignition at 550 C followed by HCl (1.0M)	1 16	Residual organic P
8	Na_2CO_3 fusion followed by HCl (9.0M)	0.3 0.5	Residual inorganic P

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[1] after Williams et al. (1967)

Table 7. Serial extraction procedure employed for fractionation of the fulvic acid (NaOH-HCl soluble) components of lake sediments after concentration on activated carbon.

Fraction	Treatment[1]	Probable organic major extractives
A	Aqueous elutant from activated C	Low molecular weight, H_2O soluble organic compounds (simple sugars, purine bases, amino acids)
B	Acetone (90%)	Tannins
C	Distilled H_2O	Polysaccharides
D	NaOH (0.5M)	Pentose sugars, nonprotein nitrogen, organophosphorus
E	Activated C residual	Unknown

---

[1] Fraction B may be purified by evaporation of acetone, dissolution of the residue in ethanol and repeated precipitation from ethanol using ether; fraction C may be purified by repeated precipitation from aqueous solutions using acetone.

Results and Discussion

Evaluation of Analytical Techniques

The development of suitable methodology for the measurement of P compounds in bottom sediments is complicated, as in the case of soils, by a lack of knowledge of the chemical forms in which the element may be present. In the absence of this knowledge, it is not possible to precisely determine recoveries on extraction or the degree to which the compound may be altered by the extraction procedure. Therefore, for the purposes of this investigation recoveries of total inorganic P and chemically extracted P components were measured using orthophosphate amendments and elemental balances, i.e. the recovery of C or P in individual fractions as a function of total P or total C.

In general, the Williams et al. (1967) modification of the Chang and Jackson (1958) method gave satisfactory (>90%) recoveries of added inorganic P in lake sediments. However, quantities of reductant-soluble P (Treatment 4, Table 6) approached minimum detectable limits and use of the Watanabe and Olsen (1962) procedure for measurement of reductant-solubilized P as recommended by Williams et al., (1967) consistently resulted in incomplete recovery of P added at low (<50 μg/g) concentration levels. Alternatively, use of H_2O_2 as an oxidant as recommended by Chang and Jackson (1958) was time consuming and complicated by concentrations of 0.5 ppm P in reagent grade H_2O_2. A new procedure was therefore developed which involved drying of the extract (70 C), ignition (600 C) or digestion ($HClO_4$), dissolution of the ignited residue in H_2SO_4 (2 N) and colorimetric analyses of P by the method of Fogg and Wilkinson (1958). The modification allowed recoveries of added P in excess of 90% and detection of 4 μg P/g of sediment.

It should be emphasized that the entire P mineral fractionation scheme is based on known solubilities of model compounds and that dissolution of discrete mineral forms by each solvent is not possible in the complex lake sediment systems. The results should therefore be used only as an indication of the mineral types which may be present. However for development of chemical control measures it should prove useful to know the relative chemical solubilities of the mineral components. Due to the extensive effort required to complete the P mineral fractionation, analyses were limited to samples from the 1969 season when much of the seasonal variation occurred.

Recovery of organic C in the benzene-ethanol, humate and fulvate fractions ranged from 65.0 to 83.2% of the total sediment organic C content. Recovery of organic P in these fractions ranged from 36.8 to 51.2% of sediment organic P content. The unrecovered C and P were largely present in the sediment as residuals not soluble in the solvents employed (Table 8). Recoveries of extracted sediment organic P, organic P present as residuals in the silica fraction removed by precipitation during the extraction, and as residuals in the sediments ranged from 89.0 to 101.8% of total organic P. Thus, little organic P was subject to hydrolysis by the solvents employed and a relatively large fraction of the sediment organic P was nonextractable. This latter fraction is likely quite stable and would contribute little to P release from sediments.

When published methods for determining inositol hexaphosphate in soils were applied to soils, insufficient inositol hexaphosphate was recovered for reliable quantitative analysis. Incomplete recoveries of inositol hexaphosphate during separation on the anion exchange resins, chemical purification, and extraction from lake sediments cummulatively reduced total recovery to levels incompatable with quantitative analysis. Therefore, new methods and ways to improve the analysis at each of these stages were investigated.

The recovery of a known quantity of inositol hexaphosphate from an anion exchange resin (Smith and Clark, 1952) by gradient elution with increased concentration of HCl is outlined in Figure 5. It is evident that complete recovery of inositol hexaphosphate from the column may be obtained by this method. However, large volumes of HCl are required over a relatively long time period (flow rate 1 ml/minute) to obtain a single analysis. In order to reduce the analytical time required, recovery was measured in a comparable manner using the method of Caldwell and Black (1958). This method involved elution of the inositol hexaphosphate with 1.4 N HCl only after removal of inorganic P from the column using 0.85 N HCl. The method allowed complete recovery of inositol hexaphosphate from the column without use of large volumes of eluent, (Figure 6).

Amendments of the combined HCl and NaOH sediment extracts, after chemical purification, with a known quantity of inositol hexaphosphate followed by column separation of the compound (Caldwell and Black, 1958) resulted in over 95% recovery of P added as inositol hexaphosphate after elution with 1500 ml of 1.4 N HCl (Figure 7). Thus, the presence of sediment

Table 8. Distribution and recovery of organic phosphorus in organic extractives and residual components of Howard Bay sediments.

Sample designation[2]	Organic P[1]				
	Silica fraction	Sediment residual	Sum of organic extractives[3]	Untreated sediment	Recovery
	----------------------	µg/g	----------------------	----------------------	%
H-1	43	97	282	317	89.0
H-2	54	96	276	271	101.8
H-3	45	88	258	290	89.0
H-4	91	116	348	382	91.1

[1] Based on oven dry 60 C weight

[2] Table 1

[3] Sum of organic P in benzene-ethanol, humic acid and fulvic acid fractions

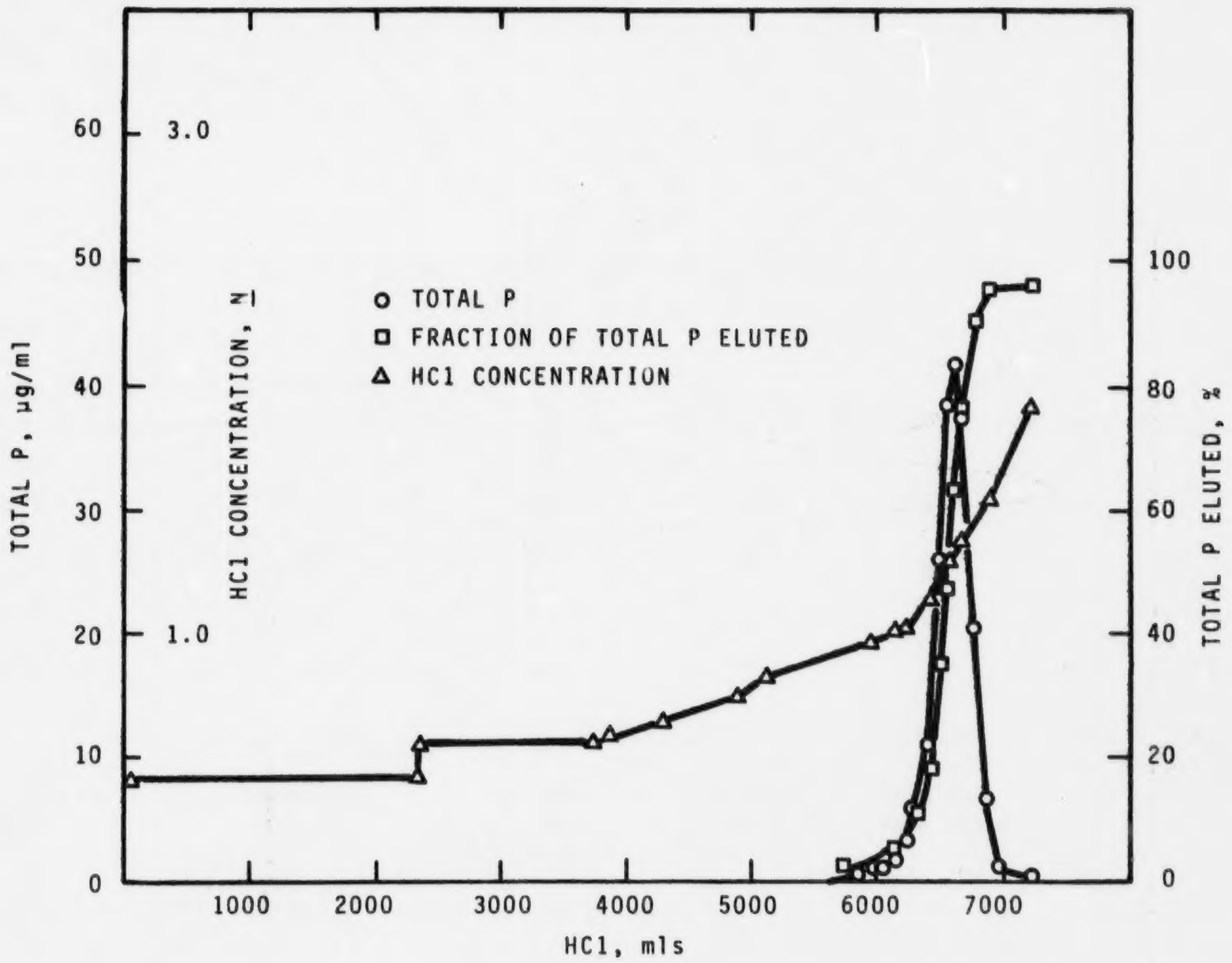

FIGURE 5. RECOVERY OF INOSITOL HEXAPHOSPHATE FROM AN ANION EXCHANGE RESIN BY GRADIENT ELUTION WITH INCREASING CONCENTRATIONS OF ACID.

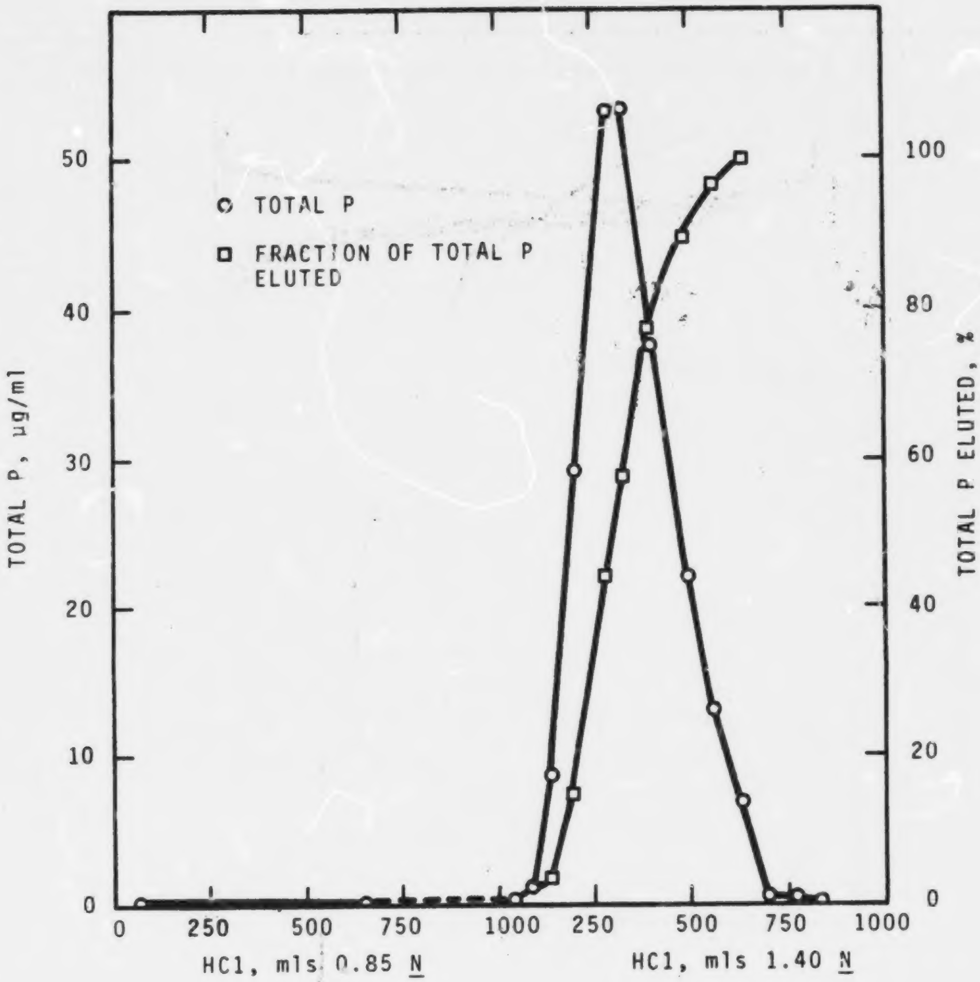

FIGURE 6. RECOVERY OF INOSITOL HEXAPHOSPHATE FROM AN ANION EXCHANGE RESIN BY ELUTION WITH ACID AT TWO CONCENTRATION LEVELS.

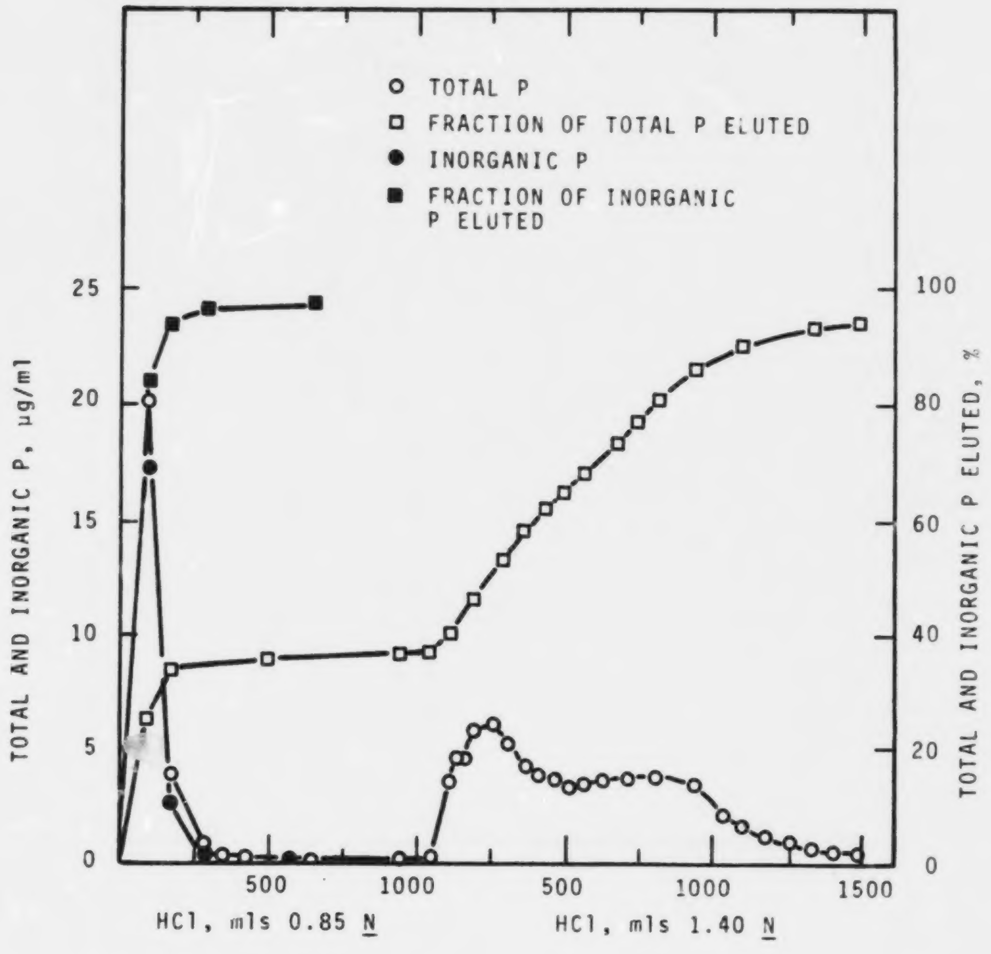

FIGURE 7. RECOVERY OF INOSITOL HEXAPHOSPHATE FROM SEDIMENT EXTRACTS USING ANION EXCHANGE CHROMATOGRAPHY.

extractives caused in a marked increase in elutart required to remove P, likely as inositol hexaphosphate from the column. The P added as inorganic P was quantitatively removed (recovery 95.6% from the column by prior elution with 0.85 N HCl). The technique proved highly replicable and consistently allowed over 95% recovery of P added as inositol hexaphosphate. Amendment of sediments with inositol hexaphosphate followed by chemical extraction, chemical purification and column separation resulted in similarly high recoveries of added inositol hexaphosphate phosphorus. Thus, analyses of sediments for inositol hexaphosphate may now be undertaken with reasonable confidence. It should be noted, however, that further methodological refinement is required. To insure the identity of separated inositol hexaphosphate in sediment extractives, the C:P ratio of the material eluted from the column at the inositol hexaphosphate position on the chromatograph must be determined. In addition, recoveries of inositol hexaphosphate from the anion exchange resin were occasionally reduced by an amorphorus $Al(OH)_3$ precipitate which formed during chemical purification and precipitation of the inositol hexaphosphate Fe salt at pH 1.8.

Seasonal Changes in Sediment Inorganic P Components

The distribution of P in the principal P mineral fractions of Upper Klamath Lake is summarized in Table 9 and further illustrated in Figures 8, 9 and 10. These data help evaluate (*i*) the potential of procedural artifacts created by the influence of chemical treatments on subsequent measurements during serial extraction and (*ii*) the effect of changes in concentrations of individual minerals or groups of minerals on changes in total inorganic P observed throughout the year. The latter objective was deemed particularly important to the identification of minerals significant in supplying P for phytoplankton growth.

The concentrations of P in the NH_4F and residual organic P fractions of Howard Bay (Table 9; Figure 8) increased markedly from spring to fall whereas the NaOH (0.1 M) fractions exhibited a marked decrease from May to June followed by a slight increase to October.

As in the case of Howard Bay, the Buck Island sediments (Table 9; Figure 9) exhibited an increase in residual organic P with time, but this was not accompanied by an increase in the NH_4F-P. The extractable P in the NaOH (0.1 M) fraction of Buck Island sediments also decreased with time. This decrease was accompanied by a decrease from May to June of $Na_2S_2O_4$ - $Na_3C_6H_5O_2$ and NaOH (1.0 M) P forms.

Table 9. Distribution of phosphorus in inorganic phosphorus fractions of Upper Klamath Lake sediments.

Sample designation[1]	P extracted[2] with									
	NH_4Cl (0.5M)	NH_4F (0.5M)	NaOH (0.1M)	NaS_2O_4 (0.1M) $Na_3C_6H_5O_2$ (0.3M)	NaOH (1.0M)	HCl (0.5M)	HCl (1.0M)	HCl Total	Ignition-HCl (1.0M)	Na_2CO_3 fusion HCl (9.0M)
	µg/g									
H-1	5	30	111	72	20	21	0	21	2	40
B-1	6	47	131	109	25	22	0	22	3	67
P-1	8	41	109	36	17	43	0	43	8	90
H-2	5	67	25	56	22	18	15	33	54	106
B-2	5	54	59	44	7	21	8	29	54	70
P-2	5	55	54	--	5	23	17	40	30	86
H-3	13	62	28	22	16	18	6	24	44	55
B-3	6	45	47	39	20	23	6	29	45	55
P-3	4	50	17	35	21	43	10	53	44	66
H-4	7	107	37	46	31	16	7	23	69	54
B-4	10	50	23	57	29	26	7	33	61	55
P-4	4	38	26	40	32	33	8	41	59	55
H-5	10	115	67	66	32	23	9	32	96	95
B-5	2	39	25	40	27	26	9	35	65	60
P-5	2	47	26	37	27	44	10	54	60	64

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[1] Table 1

[2] Table 6

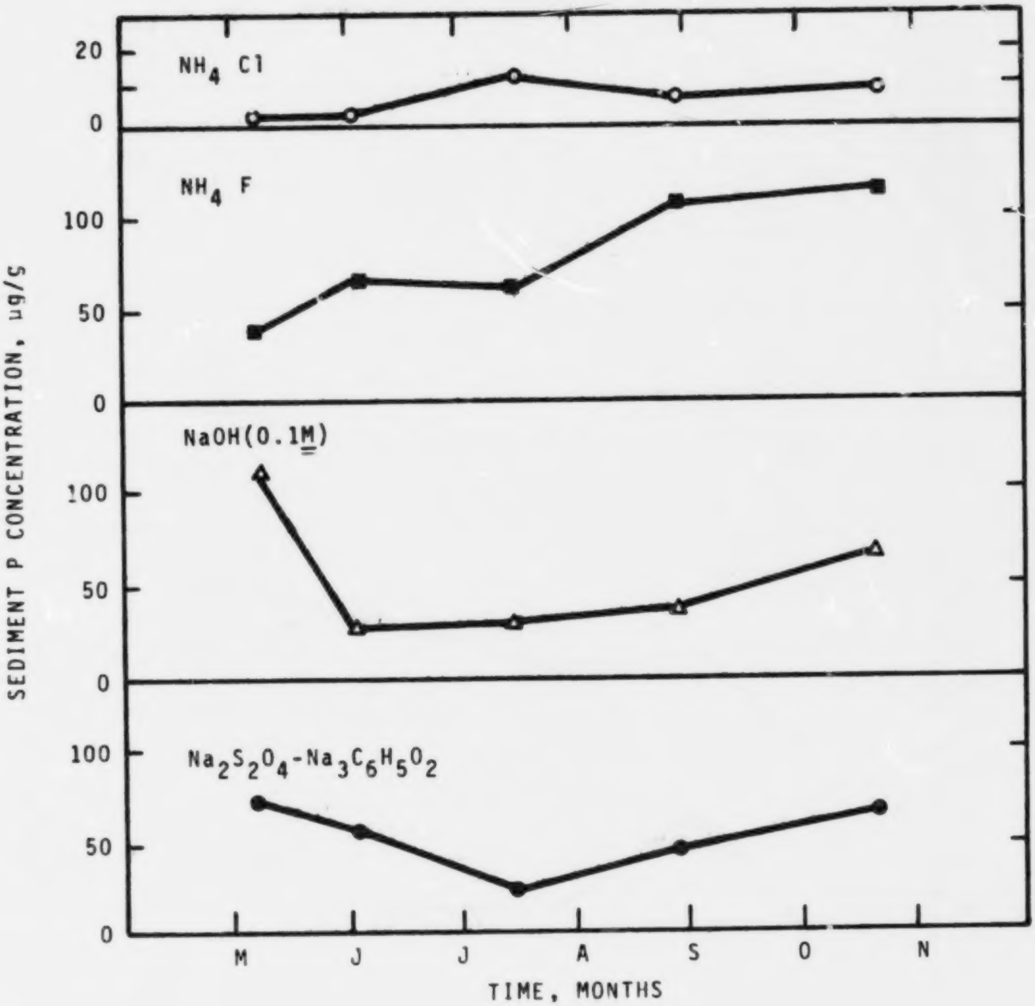

FIGURE 8a. MONTHLY DISTRIBUTION OF PHOSPHORUS IN INORGANIC PHOSPHORUS FRACTIONS OF THE SEDIMENTS OF HOWARD BAY, UPPER KLAMATH LAKE, OREGON.

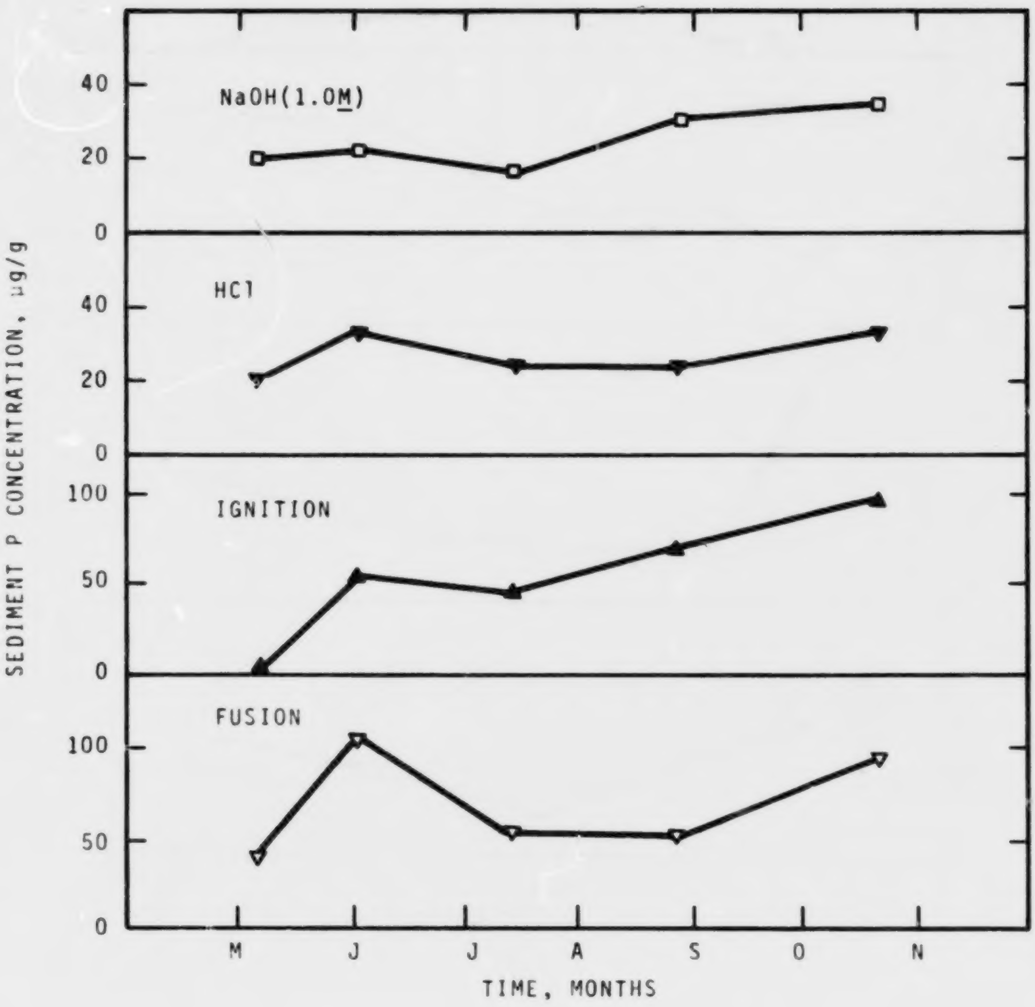

FIGURE 8b. MONTHLY DISTRIBUTION OF PHOSPHORUS IN INORGANIC PHOSPHORUS FRACTIONS OF THE SEDIMENTS OF HOWARD BAY, UPPER KLAMATH LAKE, OREGON.

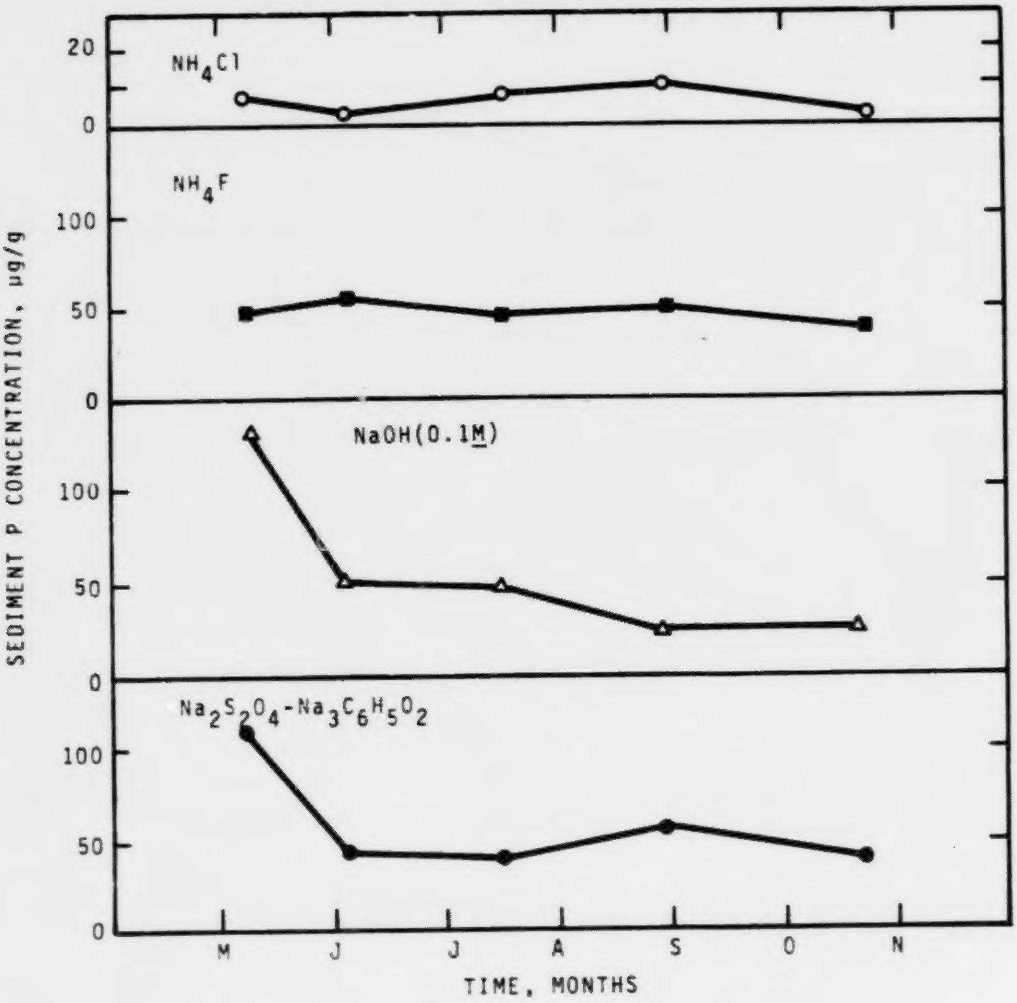

FIGURE 9a. MONTHLY DISTRIBUTION OF PHOSPHORUS IN INORGANIC PHOSPHORUS FRACTIONS OF THE SEDIMENTS NEAR BUCK ISLAND, UPPER KLAMATH LAKE, OREGON.

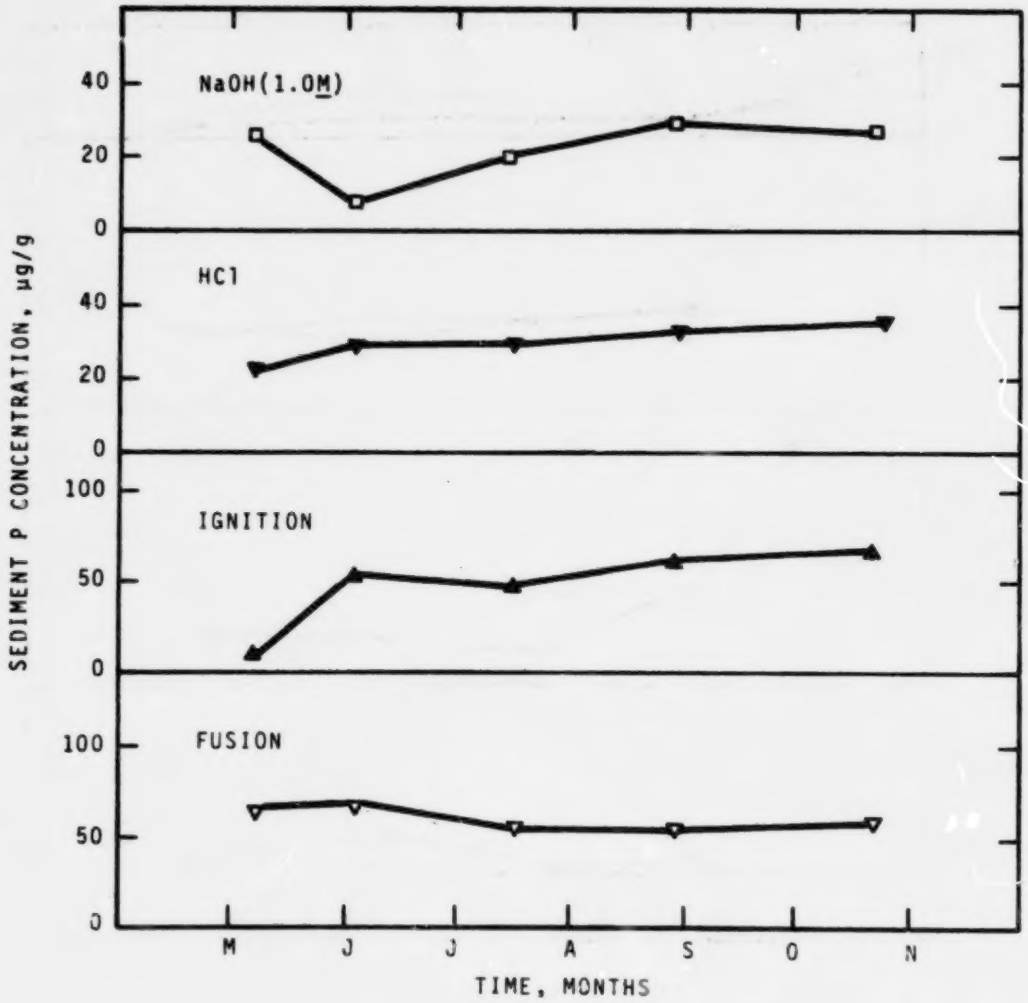

FIGURE 9b. MONTHLY DISTRIBUTION OF PHOSPHORUS IN INORGANIC PHOSPHORUS FRACTIONS OF THE SEDIMENTS NEAR BUCK ISLAND, UPPER KLAMATH LAKE, OREGON.

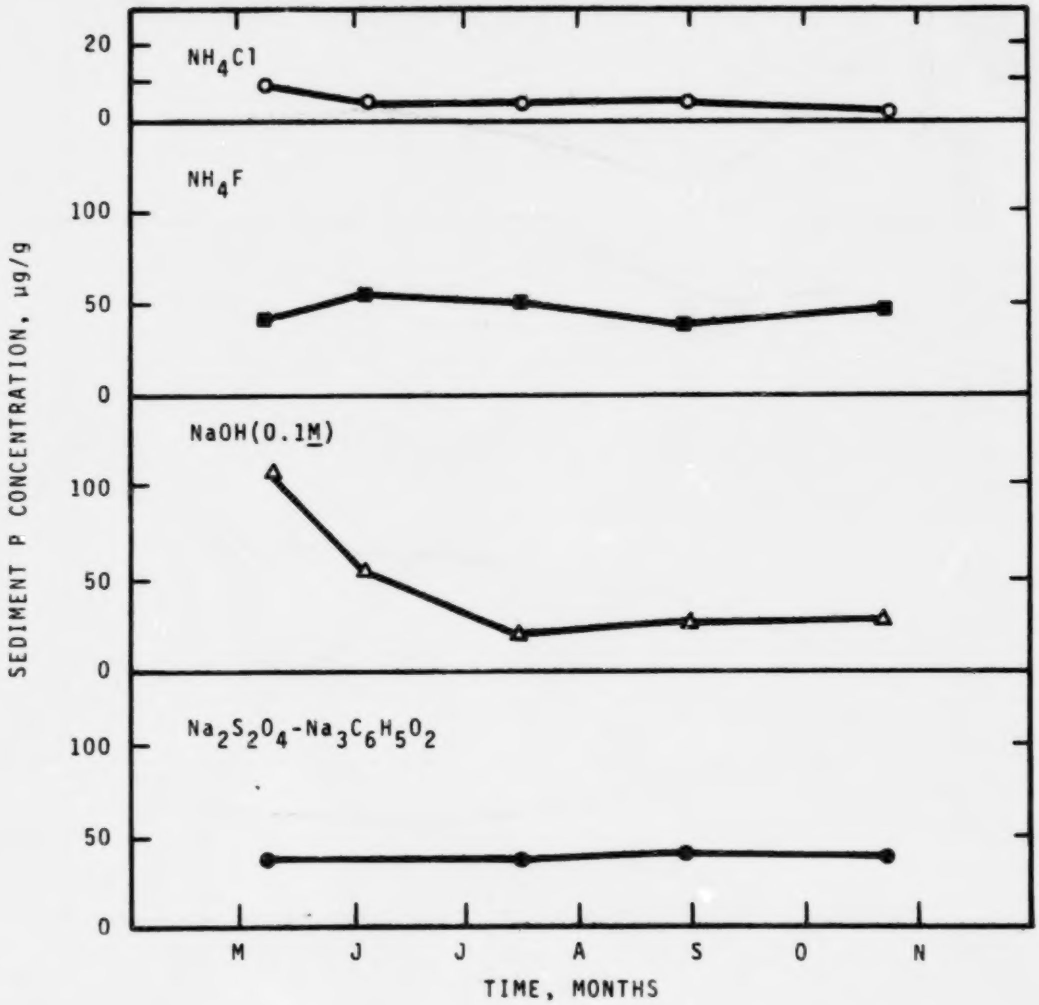

FIGURE 10a. MONTHLY DISTRIBUTION OF PHOSPHORUS IN INORGANIC PHOSPHORUS FRACTIONS OF THE SEDIMENTS OF PELICAN MARINA, UPPER KLAMATH LAKE, OREGON.

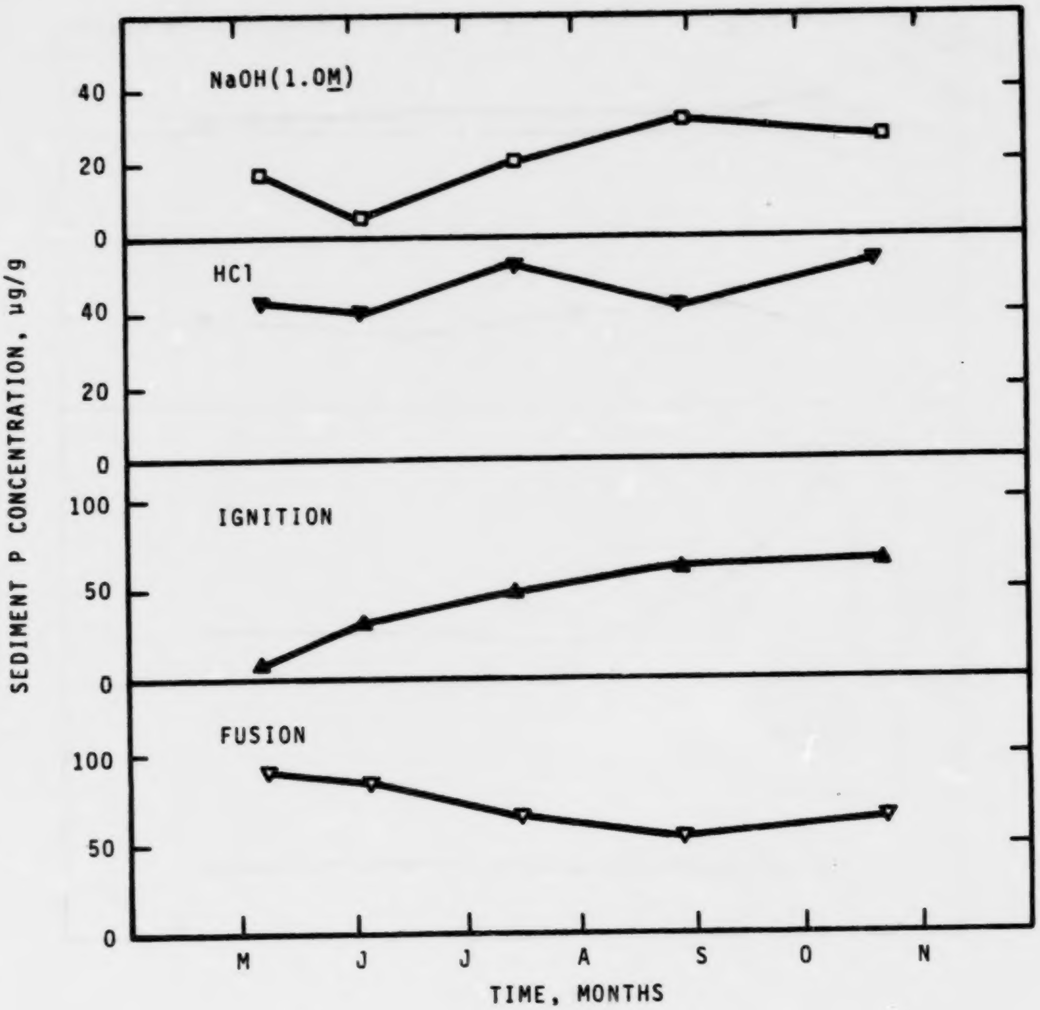

FIGURE 10b. MONTHLY DISTRIBUTION OF PHOSPHORUS IN INORGANIC PHOSPHORUS FRACTIONS OF THE SEDIMENTS OF PELICAN MARINA, UPPER KLAMATH LAKE, OREGON.

The Pelican Marina sediments increased in NaOH (0.1 M)-P and residual organic P from May to October. As in the case of the other sediments, NaOH (0.1 M)-P decreased over this time period.

Two changes in mineral P over the season common to all sediment locations were (*i*) an increase in residual organic P and (*ii*) a marked decrease in NaOH (0.1 M) soluble P. Howard Bay sediments, which showed the largest seasonal variation in total and inorganic P, exhibited marked increases in NH_4F-P but this was not common to sediments from other locations.

Increases in residual organic P in the cases of Howard Bay and Buck Island sediments appeared to reflect overall increases in sediment total organic P (Figure 3). However in the Pelican Marina sediments total organic matter P decreased, yet residual organic P increased. The increase in residual organic P was accompanied by a decrease in the next fraction, i.e. the residual inorganic P fraction. Perhaps this results from incomplete solubilization of residual organic P which was subsequently measured on fusion. It should also be noted that organic matter is solubilized by NaOH, the solvent used for extraction of various forms of Fe-P. Decreases in the Fe-P fraction may have been due in part to incomplete extraction of organic P which later was recovered in the residual organic P fractions. However, increases in the residual organic P fraction could not account entirely for the marked decreases in the Fe-P fraction during the season and this decrease must therefore be considered real in part.

The sediments of Howard Bay (Figure 3) exhibited the greatest changes in inorganic P during the 1969 and 1970 seasons. An initial reduction in sediment total and inorganic P early in the spring followed by increases in total and inorganic P in the summer and fall have been previously attributed (Section IV, A) to biological uptake of P early in the season followed by the deposition and partial mineralization of biological tissue later in the season. Evaluation of the changes in P mineral components for Howard Bay over this period indicates that the principal minerals resulting in a decrease of sediment P were in the NaOH (0.1 M) or Fe-P fraction. The P in this fraction gradually increased during late summer and fall, but increases in inorganic P during this period were due primarily to increases in minerals in NH_4F or Al-P fraction. Minerals in the Fe-P fraction appeared to supply P to solution during biological growth with a reduction in the Fe-P fraction (Figure 8) amounting to 86 μg P/g of sediment from May to June (H1 and H2, respectively; Table 9) compared to a total reduction in inorganic P (Treatments 1-6; Tables 6, 9) of 60 μg P/g (Treatments 1-6 have been taken, Section IV, as representing the labile inorganic P fraction). The differences between 86 μg P/g and 60 μg P/g appeared to be accounted for by relative increases in the NH_4F (Al-P) and HCl (Ca-P) fractions.

Minerals in the NH_4F fraction accounted for a major portion of the increase in inorganic P from July to October with smaller contributions from the various Fe-P fractions.

It is difficult, on the basis of individual sample site comparisons, to estimate the extent to which changes in the inorganic P fractions contributed to changes in the total inorganic P fraction for all sediment locations. In order to obtain a gross estimate of this effect, a regression analysis of P concentrations in individual extracts against total inorganic P was employed. It should be noted, however, that the results are indicative of trend only since the inorganic P components are inherently related to total inorganic P of which they are a fraction. To undertake the regression analyses, several assumptions were made: (*i*) changes in the Al-P, Fe-P and Fe, Al-oxide occluded Fe-P, Al-P fractions (Treatments 2, 3, 4; Table 6) which are of the largest magnitude would have the greatest effect on total inorganic P and (*ii*) the inorganic P treatments are independent statistically and have equal variances. With these assumptions it is possible to state that total inorganic P regressed against the sum of 3 fractions will have an expected r value of 0.707. Hence the degree that the r value exceed this "expected" value is a measure of the extent of correlation to total relative to the remaining 3 fractions. The results are summarized in Table 10. Based on the above assumptions, Treatments 2, 3, 4, representing forms of Al-P, Fe-P and Fe and Al oxide occluded P accounted for approximately 85% of the variance in total inorganic P occurring at all sampling locations throughout the year.

Distribution of C and P in Sediment Organic Fractions

Although the physicochemical properties of the sediment organic matter are likely altered upon extraction, particularly when alkali is employed as an extractant (Bremner, 1950), initial definition of sediment P components on the basis of solubility may prove useful in designing remedial techniques to minimize release of P from sediments. In addition, changes in the concentration of those components which may occur in response to changes in

Table 10. Summary of the regression of individual extractant phosphorus concentrations against total inorganic sediment phosphorus for all Upper Klamath Lake locations sampled during a single season.

Extractant	Degrees of freedom	Intercept	Regression coefficient	Standard error of regression coefficient	Correlation coefficient[1]	Variation of total inorganic P attributable to changes in extractant P
Sum of Treatments 2,3,4 (Table 6)	13	130	1.003	0.120	0.923[1]	85.2

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[1] Significant at the $p < 0.05$ level

limnological conditions may provide insight into the chemical nature of the labile sediment organic components.

As in the case of the inorganic P fractionation, the organic extractions and analysis are highly time-consuming and therefore the number of samples which could be analyzed was limited. Sediments from Howard Bay were selected for this phase of the study because changes in the sediment organic P content occurred concommitantly with changes in limnological conditions.

Carbon. The distribution of organic C in the benzene-ethanol, humic acid and fulvic acid fractions of Howard Bay sediments during the monitoring period ranged from 6.9 to 11.5%, 7.8 to 10.3% and 49.8 to 66.0%, respectively (Table 11). Thus, the bulk of the recovered organic C was in the fulvic acid fraction and therefore soluble in both alkali and acid. Changes in the concentrations of C in this fraction with time were, however, not related to changes in sediment organic C.

The concentrations of C in the benzene-ethanol fractions decreased from May to June and subsequently increased from July to August corresponding to similar reductions in sediment organic C and accounting, respectively, for 20.3% and 38.0% of the reduction in sediment organic C from May to June and the increase in sediment organic C from July to August (Table 4). Organic materials likely contained in this fraction, i.e. lipids, fats and waxes derived from fresh or relatively undecomposed organic detritus, should serve as relatively available energy sources for the sediment microfloral population under the conditions of increased temperatures in the spring. As phytoplankton growth declines in late summer, the rate of deposition of these materials may exceed the rate of decomposition resulting in an increase in sediment concentration.

Humic acid C (Table 11) was quite stable during the year accounting for a relatively constant proportion of total sediment C. If, analagous to soil humic acid, sediment humates consist of polymers of aromatic compounds, microbial stability of this fraction may be expected.

The major portion of fulvic acid C (Table 11, 12) was present in subfractions B, C, and D (Table 7). Investigations with a diverse series of soils including a peat (Forsyth, 1947) indicated that in soil systems only a small fraction of the organic matter in the fulvic acid fraction was eluted through charcoal with water (Fraction A, Table 7). Most of the organic matter consisted of more complex substances which were present in

Table 11. Seasonal distribution of organic carbon in the benzene-ethanol, humic acid and fulvic acid fractions of lake sediments.

		Organic C^2 in							
		Benzene-ethanol fraction		Humic acid fraction		Fulvic acid fraction		Total organic C recovered	
Sample designation[1]	Sediment organic C content	Absolute	Fraction of total	Absolute	Fraction of total	Absolute	Fraction of total	Absolute	Fraction of total
	mg/g	mg/g	%	mg/g	%	mg/g	%	mg/g	%
H-1	79.30	7.88	9.9	7.24	9.0	33.50	57.4	48.62	76.4
H-2	63.80	4.73	7.4	4.99	7.8	31.80	49.8	41.52	65.0
H-3	65.60	4.50	6.9	6.77	10.3	43.40	66.0	54.57	83.2
H-4	77.30	8.94	11.5	6.80	8.8	43.60	56.4	59.34	76.7

[1] Table 1

[2] Based on oven-dry (60 C) weight

subsequent fractions. By analogy to soil systems (Forsyth, 1947), subfractions B, C, and D likely contained materials of relatively high molecular weight including phenolic glycosides (B), polysaccharides (C) and mixtures of N compounds and pentose sugars.

Fraction D contained the largest quantities of C throughout the season and increased from < 40% of the fulvic acid C in May and June to over 60% in July and August (Table 12). In characterizing subfraction D components isolated from soil, Forsyth (1947) employed simple dialysis followed by electrodialysis to remove the alkali and concentrate the extract. The bulk of the material formed at the anode. The material did not give positive protein tests but contained the largest quantity of N and considerable quantities of P.

Phosphorus. As in the case of organic C, the fulvic acid fraction contained most of the recovered organic P (Table 13) ranging from 26.2 to 32.5% of sediment organic P. Benzene-ethanol soluble P ranged from 2.9 to 4.1% of organic P and varied directly with it. Humic acid organic P accounted for 7.8 to 12% of the sediment organic P. Although there was a marked decrease in humic acid P concentration from May to June as in the case of the other extractants, humate P remained constant from June to August. Taken together, organic P in the fulvate, benzene-ethanol and humate fractions accounted for 35% of the reduction in organic P from May to June and 20% of the increase from July to August with the unrecovered fraction (Table 8) accounting for 65% of the decrease from May to June and organic P in the silica and sediment residual fractions (Table 8) accounting for much of the increase from July to August.

In general, changes in sediment organic P could not be attributed to changes in organic P concentration in any single fraction. Benzene-ethanol, fulvate and humate fractions together accounted for less than 50% of the total organic P. Approximately 50% of the sediment organic P consisted of organic P in the silica fraction or as nonextractable sediment residual (Table 8). The organic P in the silica fraction likely consisted of silica occluded organic matter from both the fulvic and humic fractions. The unextractable organic P residual in the sediment may have been present as highly stable mineral organic P complexes.

In contrast to sediment organic C (Table 12) and soil organic matter (Forsyth, 1947), which were present in highest concentrations in fulvic acid subfractions B, C and D, the largest

Table 12. Seasonal distributions of organic carbon in components of the fulvic acid fraction of lake sediments.

Sample designation[1]	Fulvic acid organic carbon	Distribution of organic carbon in fractions[2,3]			
		A	B	C	D
	mg/g	%			
H-1	45.49	6.1	28.1	26.4	39.4
H-2	31.75	5.3	32.9	25.5	36.3
H-3	43.26	1.8	25.2	13.0	60.0
H-4	43.63	3.9	15.2	12.2	68.7

[1] Table 1

[2] Table 7

[3] Based on oven-dry (60 C) weight

proportion of the fulvic acid organic P (Table 14) was present in subfraction A which contained water soluble materials likely of relatively low molecular weight. Only organic P in the water soluble and consequently the most labile subfractions A and C varied on an absolute basis with seasonal changes in sediment organic P (Table 13). If it is necessary to predict changes in sediment organic P it would appear that these chemical fractions would be a useful point of departure for future research.

Isomers of inositol hexaphosphate are believed to constitute the bulk of the organic P in soils. It is likely that inositol hexaphosphate present in soils is derived largely from terrestrial plants which contain considerable quantities of the substance as the Ca-Mg salt, phytin. It is also known that certain soil microorganisms may synthesize inositol hexaphosphate but little information is available regarding the quantity of inositol hexaphosphate formed in this manner in soils or sediments.

Phytoplankton, the likely principal source of organic P to sediments of eutrophic lakes contains only small quantities of inositol hexaphosphate. Thus if inositol hexaphosphate is present in sediments in significant quantities it must result from microbial synthesis or be of terrestrial origin. If of terrestrial origin, it may serve as a useful indicator of terrestrial sources of organic P.

At soil or sediment pH values between pH 1.5 and approximately pH 4.0, inositol hexaphosphate may be expected to be relatively insoluble as Fe or Al salts. Above the pH range of 5.5 to 6.5 inositol hexaphosphate is likely insoluble as Ca or Mg salts (Jackman and Black, 1951). At pH values between 4.0 and approximately 6.5 finite solubility of inositol hexaphosphate, and subsequent release of the material to solution from the solid phase, may be expected. The extent of release will be highly dependent upon water and sediment properties. If inositol hexaphosphate represents a significant portion of the sediment organic P fraction, remedial measures based on the alteration of sediment pH or sediment concentration of Fe-Al or Ca-Mg might be successful in reducing the release of inositol hexaphosphate to solution. The factors influencing the mineralization of inositol hexaphosphate in sediments would also be deserved of detailed attention. In the present studies a suitable method was developed for estimation of inositol hexaphosphate in sediments. Inositol hexaphosphate was not present in detectable (< 10 μg/g of sediment) quantities

Table 13. Seasonal distribution of organic phosphorus in benzene-ethanol, humic acid and fulvic acid fractions of lake sediments.

Sample designation[2]	Sediment organic P content	Organic P[1] recovered in					
		Benzene-ethanol fraction		Fulvic acid fraction		Humic acid fraction	
		Absolute	Fraction of total organic P	Absolute	Fraction of total organic P	Absolute	Fraction of total organic P
	µg/g	µg/g	%	µg/g	%	µg/g	%
H-1	317	13	4.1	89	28.1	40	12.6
H-2	271	10	3.7	88	32.5	28	10.3
H-3	290	9	3.1	84	23.0	32	11.0
H-4	382	11	2.9	100	26.2	30	7.9

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[1] Based on oven-dry (60 C) weight

[2] Table 1

Table 14. Seasonal distribution of organic phosphorus in components of the fulvic acid fraction of lake sediments.

Sample[1] designation	Fulvic acid organic P content	Distribution of organic C in fractions[2,3]				
		A	B	C	D	E
	µg/g	%				
H-1	89	49.4	18.0	13.5	7.9	11.2
H-2	88	36.4	11.4	3.4	9.1	39.7
H-3	84	31.0	20.2	7.1	13.1	28.6
H-4	100	36.0	9.0	17.0	12.0	26.0

[1] Table 1

[2] Based on oven-dry (60 C) weight

[3] Table 7

in Upper Klamath Lake sediments. Future investigations might be designed to determine its concentration in a broad range of sediments and its importance as an indicator of terrestrial contamination or as a supplier of P to solution.

SECTION V

POTENTIAL FOR RELEASE OF PHOSPHORUS FROM SEDIMENTS -- LABORATORY INVESTIGATIONS

The P status of Upper Klamath Lake sediments changed markedly at the Howard Bay location as limnological conditions changed with the seasons. Less pronounced changes occurred at the Buck Island and Pelican Marina sampling locations than at Howard Bay. These changes in P status provided impetus for extension of the field studies to the laboratory. However, it was also recognized that due to the high concentration of P in the sediment relative to the water, gross changes in sediment P status need not occur in order for sediments to significantly influence water composition. Therefore laboratory studies were undertaken to more precisely define the rate and extent of P release from sediments. Inherent in this objective was the development of suitable methodology for the incubation and study of sediments in the laboratory. The laboratory investigations may be divided into two sections dealing with (*i*) development of methods for measurement of P release and algal growth potential and (*ii*) measurement of factors influencing the release and algal growth potential of sediment P.

A. LABORATORY METHODS FOR MEASUREMENT OF PHOSPHORUS RELEASE AND ALGAL GROWTH POTENTIAL

Initially emphasis was placed on development of laboratory techniques for measurement of P release which allowed the manipulation of the parameters of sediment and water composition, pH, aeration and temperature. A dialysis system appeared to offer the greatest versatility in that the sediment and water could be partitioned, subjected to individual treatment and the effect on P equilibria measured.

Several prototypic methods were developed and evaluated as to efficacy of measurement of the potential P release from sediments and of the influence of environmental parameters on P release. These included (*i*) a dialysis method involving the equilibration of sediment in a cellulose acetate membrane with distilled water, (*ii*) a dialysis method in which sediment and water in glass half-cells were partitioned with a 0.45 μ filter and (*iii*) a sediment-resin system based on the soils method of Cooke (1966) in which P was taken up directly by anion exchange resin placed in the moist sediment.

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Membrane Dialysis System

As an initial test of the dialysis concept for the measurement of P sediment-water equilibria, a cellulose acetate membrane system was designed.

Materials and Methods

Moist Howard Bay sediment samples were sealed in cellulose acetate dialysis tubing (4.1 cm in dia) and immersed in distilled water (600 ml). Aliquots (15 ml) were removed from the water outside the membrane at periodic intervals and analyzed for orthophosphate. After sampling, a volume of water equal to the aliquot removed was re-added to maintain a constant volume. The treatments were maintained in the dark at 23 ± 2 C.

Results and Discussion

The release of P from Howard Bay sediments amounted to 15.6 μg P/g of moist sediment. Release represented a small fraction of total inorganic P. However P release amounted to approximately three times the quantity of readily extractable (NH_4Cl) P for this sediment. Thus, P dissolution occurred. A second, more extensive experiment was therefore undertaken utilizing this system. The results of the second experiment are reported in Section V, B. Those studies indicated that the cellulose acetate was visually degraded after approximately 15-20 days and long-term incubation or precise control of pore size were not possible with this system.

Filter Dialysis System

To overcome problems of membrane decomposition and provide more precise control of membrane pore size, an alternative to the cellulose membrane technique was devised. The new apparatus (Figure 11), consisted of two pyrex glass half-cells separated by a membrane filter supported on two fritted glass filters (coarse pore size) incorporated into each half-cell. The half-cells, one containing sediments and the other containing water, were bound together under spring tension and gently shaken. The water cells were periodically analyzed for total and inorganic P. Aliquots removed for analysis were replaced with a fresh increment of distilled water. In later experiments the entire water volume was removed from the half-cell and replaced with distilled water.

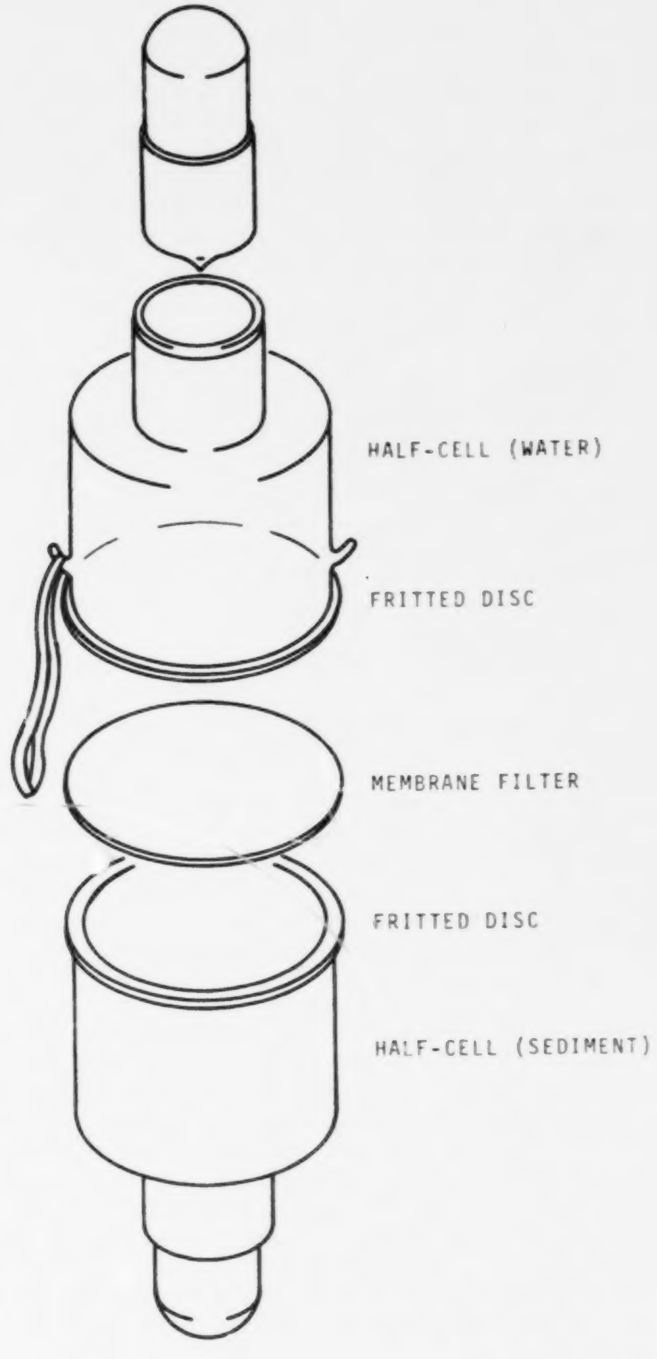
HALF-CELL (WATER)
FRITTED DISC
MEMBRANE FILTER
FRITTED DISC
HALF-CELL (SEDIMENT)

FIGURE 11. SEDIMENT DIALYSIS APPARATUS

The new dialysis system was evaluated as to the rate of diffusion of P across the fritted glass filter and the effect on diffusion rate of restriction of particle size to 0.45 μ. In later experiments described in Section V, B, the extent of resorption of P from the water cells by the sediments and the influence of composition (distilled water vs. dilute salt media) on diffusion rate were evaluated.

Materials and Methods

To determine the rate of P diffusion across the 0.45 μ membrane used in the dialysis system, P (20.38 μg/ml) was added to one half-cell, normally employed for sediments but containing water. The rate of diffusion into the second half-cell, containing distilled water only, was monitored. The results were expressed as a percentage of complete diffusion (an equilibrium concentration of 50% of the P added to the "sediment" half-cell). To determine the extent of diffusion across the fritted disk alone, the above experiment was repeated in the absence of the filter.

Results and Discussion

Diffusion of P through the 0.45 μ filter separating the dialysis cells was relatively slow: only 24.1% after 20 days (Table 15). Thus, diffusion must be considered a factor limiting the rate of sediment P release determined using the dialysis systems. Removal cf the 0.45 μ filter leaving only the fritted discs separating the cells resulted in complete equilibration in 48 hours. Thus, diffusion rate would not be limiting in experiments in which P release could be measured in the absence of the filter, but sterility of the water half-cell could not be maintained.

Use of the filter dialysis system has several advantages compared to the cellulose acetate dialysis tubing employed previously. For examples, (*i*) the filter is not biodegradable under the conditions employed and (*ii*) the filter pore size is precisely defined and may be changed to allow accurate measurements of the type and extent of particulate diffusion from the sediment, (*iii*) sediments and waters may be initially treated separately as required allowing evaluation of a broad range of parameters and (*iv*) the water half-cell may be maintained in a sterile condition while dialyzing against a non-sterile sediment provided the filter pore size is < 0.45 μ.

Table 15. Equilibration of phosphorus between water cells separated by a 0.45 μ filter in the dialysis system.

Incubation time	P diffused[1] through membrane
days	% of complete diffusion[2]
1	2.0
2	4.9
3	7.3
4	9.7
5	11.4
6	14.0
7	17.0
8	18.4
10	21.7
14	22.3
20	24.1

[1] Initial concentration in P half-cell 20.38 μg/ml

[2] Complete diffusion was taken as an equilibrium concentration of 50% of the P added

Direct Equilibration With an Anion Exchange Resin

To devise a simple technique which may be useful on a routine basis for estimation of the potential for P release from sediments, a method previously reported for the evaluation of the kinetics of P release from soils (Cooke, 1966) was modified and applied to sediment systems. The modified method simply involved direct equilibration of moist sediments with an anion exchange resin, separation of the resin from the sediment sample at regular time intervals and displacement and measurement of the P on the resin. The technique offers the advantages of (*i*) simplicity, (*ii*) measurement of the kinetics of P release and (*iii*) measurement of potential release since a P sink is provided shifting sediment-solution P equilibrium in the direction of the solution phase. However, in order to use the method, the optimum conditions for measurement had to be determined. Preliminary tests were therefore conducted to determine (*i*) the best method for incubating and subsequently separating the resin from the sediment, (*ii*) the efficiency of P uptake by the resin, and (*iii*) the optimum moisture to sediment and resin to sediment ratios. After initial testing, an evaluation was made of the release of P in the new system as related to release in the dialysis system, in the presence and absence of anion exchange resin and to algal growth potential. The results are recorded in Section V, B.

Materials and Methods

To assure the suitability of the anion exchange resin selected for release studies, an experiment was designed to test the efficiency of orthophosphate P uptake and release. Resin solutions at concentrations of 1-5 g/100 ml were spiked with 123 to 12280 μg P and equilibrated for 17 hr. At the end of the equilibration period, the concentration of P remaining in solution was determined and the resin removed. The P on the resin was exchanged by equilibration with 100 ml of HCl (0.1 to 1.0 N) and an aliquot analyzed for orthophosphate P as previously described.

To facilitate separation of the resin from the sediments, small capsules (1.2 cm x 2.0 cm) containing resin (1.0 g) were mixed with sediments (27.5 g wet weight, 2.5 g dry weight) and 25 ml of distilled H_2O in polypropylene bottles. The system was then equilibrated (minimum 2 hr) with 50 ml of HCl (0.1 N), a satisfactory method as determined above, and the equilibration solution analyzed for P.

As a list of the influence of resin sediment ratio in the batch equilibration system, various concentrations of resins were mixed with Howard Bay sediment (27.5 g wet weight, 2.5 g dry weight) and 25 ml of distilled water in polypropylene bottles and equilibrated with gentle shaking. Periodically the sediment was decanted and the resin washed with distilled water. The washed resin was subsequently equilibrated (minimum 2 hr) with 50 ml of HCL (0.1 N) and the equilibration solution analyzed for P.

Results and Discussion

The suitability of the anion exchange resin for uptake of P from solution is exemplified by the data presented in Table 16. Complete removal of P from solution was obtained for water samples of concentrations many-fold higher than normally measured in dialysis systems (< 612 μg P). The P may be quantitatively displaced with acid and subsequently analyzed (Table 17).

Optimum release after 15 days incubation was attained at resin: sediment ratios 1:2 and 1:1 (Treatments 3 and 4, respectively, Tables 18, 19). Reduced release at a 2:1 ratio may have been due in part to a resin effect on solution pH (Table 19). Extension of incubation time to 30 days (Treatments 3, 4, and 5) resulted in additional release but at a reduced rate. The rate of release could be described by regression of the P released against the log of time (Table 20).

Measurements of total P in solution indicated that a small fraction (likely organic P) of the P released was not retained by the resin. The maximum quantities of total P in solution during the first days of incubation were approximately equivalent for all treatments. However, during the latter phases of incubation total solution P decreased in systems not containing resin. This decrease was accompanied by a reduction in solution pH which was not observed in the resin systems. The resin evidently served as a buffer maintaining a relatively constant pH.

Estimation of Algal Growth Potential

A preliminary test of the EPA Provisional method (1969) for estimation of algal growth potential was undertaken to establish (*i*) the most suitable method of algal growth measurement and (*ii*) a standard growth curve. A revised version of the Algal Assay Procedure was issued in August, 1971. This method was subsequently evaluated in a manner similar to that described below. A standard curve for the new media is included.

Table 16. Removal of orthophosphate phosphorus from solution by an anion exchange resin.

Total P added	Quantity of resin	Fate of P after equilibration P removal from solution	Fate of P after equilibration Fraction removed
µg	g	µg	%
123	1.0	123	100.0
306	1.0	303	99.0
612	1.0	597	97.5
612	1.0	591	96.6
612	1.0	592	96.7
612	1.0	592	96.7
1228	1.0	1133	92.3
3057	1.0	2558	83.7
6114	1.0	4496	73.5
12280	1.0	8113	66.1
12280	2.5	9482	77.2
12280	5.0	10430	84.9

Table 17. Acid displacement of orthophosphate phosphorus from an anion exchange resin.

Acid concentration	Total P on resin	Quantity of resin	P displaced to solution	Fraction displaced
me./ml	µg	g	µg	%
0.1	597	1.0	582	98.3
0.2	591	1.0	601	101.7
0.5	592	1.0	591	99.8
1.0	592	1.0	590	99.7

Table 18. Experimental design employed in investigations of direct uptake of phosphorus from moist sediments by different quantities of an anion exchange resin in a direct equilibration system.

Treatment number	Quantity of		Resin: sediment
	Sediment[1,2]	Resin	
	g		
1	2.5	0.25	1:10
2	2.5	0.50	1:5
3	2.5	1.25	1:2
4	2.5	2.50	1:1
5	2.5	5.00	2:1
6	2.5	0.00	

---

[1] 27.5 g wet weight (9.05% solids)

[2] After addition of 25 mls distilled H_2O, sediment solution initially a total of 45 μg total P, 32 μg inorganic P.

Table 19. Uptake of phosphorus from moist sediments[1] by an anion exchange resin as influenced by resin concentration in a direct equilibration system.

Incubation time	P in solution		Total P on resin	pH
	Total P	Inorganic P		
days	----------------------µg/g sediment-----------			
		Treatment 1		
1	23	10	12	6.6
2	22	6	50	6.8
4	24	2	101	6.7
7	39	10	132	6.8
11	44	12	136	6.6
15	48	16	196	6.8
		Treatment 2		
1	19	10	16	6.6
2	20	6	72	6.6
4	26	5	112	6.6
7	30	12	125	6.6
11	39	12	129	6.6
15	36	12	184	6.7
		Treatment 3		
1	18	10	15	6.4
2	16	0	57	6.4
4	18	2	115	6.4
7	26	8	152	6.4
11	35	13	194	6.4
15	36	14	252	6.6
18	33	12	234	6.4

Table 19 (Continued).

Incubation time	P in solution		Total P on resin	pH
	Total P	Inorganic P		
days	µg/g sediment			
	Treatment 3 (continued)			
22	32	8	245	6.6
26	36	10	256	6.8
30	34	10	308	6.8
	Treatment 4			
1	18	8	38	6.2
2	15	2	103	6.2
4	17	3	145	6.0
7	24	8	185	6.0
11	30	16	200	6.0
15	24	10	266	6.2
18	34	16	277	6.1
22	29	14	237	6.2
26	34	17	298	6.6
30	26	12	302	6.6
	Treatment 5			
1	12	4	68	6.0
2	11	2	110	5.5
4	15	4	126	5.7
7	14	4	122	5.6

Table 19 (Continued).

Incubation time	P in solution		Total P on resin	pH
	Total P	Inorganic P		
days	----------------- µg/g sediment--------			
		Treatment 5 (continued)		
11	26	16	136	5.6
15	21	8	166	5.8
18	18	7	192	5.8
22	12	6	195	6.0
26	18	12	252	6.2
30	21	12	276	6.4
		Treatment 6		
1	23	12		7.0
2	26	4		6.9
4	34	10		6.9
7	36	8		6.8
11	33	27		6.8
15	28	7		6.8
18	40	21		6.8
22	40	20		6.8
26	42	21		7.0
30	44	11		7.0

---

[1] Table 18

Table 20. Summary of regressions of phosphorus uptake by resin systems against log of time.

Treatment No.	Degrees of freedom	Intercept	Regression coefficient	Std. error of regression coefficient	Correlation coefficient
1	4	9.88	143.16	14.74	.979[2]
2	4	23.17	122.80	15.38	.970[3]
3	8	2.66	189.56	11.00	.987[2]
4	8	41.63	172.88	12.61	.979[2]
5	8	57.36	114.68	20.22	.895[2]

[1] Table 18

[2] $p < 0.001$

[3] $p < 0.01$

Methods and Materials

The algae *Selenastrum capricornutum* was employed as described by the Joint Industry/Government Task Force on Eutrophication (1969) to assay the availability of P released to solution from sediments.

To evaluate optical density (600 mμ) as a measure of algal growth response, aliquots (0.5 ml) of the culture solutions were taken during growth of the test organism and optical density measurements correlated with tentative Coulter counts and dry weight measurements at 7 incubation time intervals. Each measurement was replicated 8 to 10 times.

Standard growth curves were established over the concentration range 0.01 to 0.6 mgP/liter by amendment of the standard culture media with solutions of known P (KH_2PO_4) concentration. A standard curve for the revised method (National Eutrophication Research Program, 1971) utilizing maximum cell concentrations as an index of P concentrations in the media was developed as described above.

Results and Discussion

Optical densities of the culture media during growth of the test organism were linearly correlated with tentative Coulter counts between 60 x 10^8 and 10 x 10^9 cells/ml (Figure 12), and dry weight Figure 13). The convenient optical density measurement was utilized as an index of algal growth in subsequent studies with this media.

The growth responses of the test organism to P over the concentration ranges 0.00 to 0.08 μg/ml and 0.10 to 0.60 μg/ml are illustrated in Figure 14 and 15, respectively. The assay methods appeared sensitive to 0.04 μg/ml with the best response occurring above 0.10 μg/ml.

The revised version of the provisional bioassay method (Algal Assay Procedure Bottle Test, 1971) utilized a nutrient media of lower concentration than the original version and the direct counting method proved to be the most practical means of evaluating growth. The new media was utilized in the latter experiments described in Section V, B. With the new media, the maximum specific growth rate (μ_{max}) did not serve as an index of P concentration in solution. In fact the data indicated that μ_{max} decreased as P concentrations increased (0.05 to 0.25 μg/ml). This apparently reflected

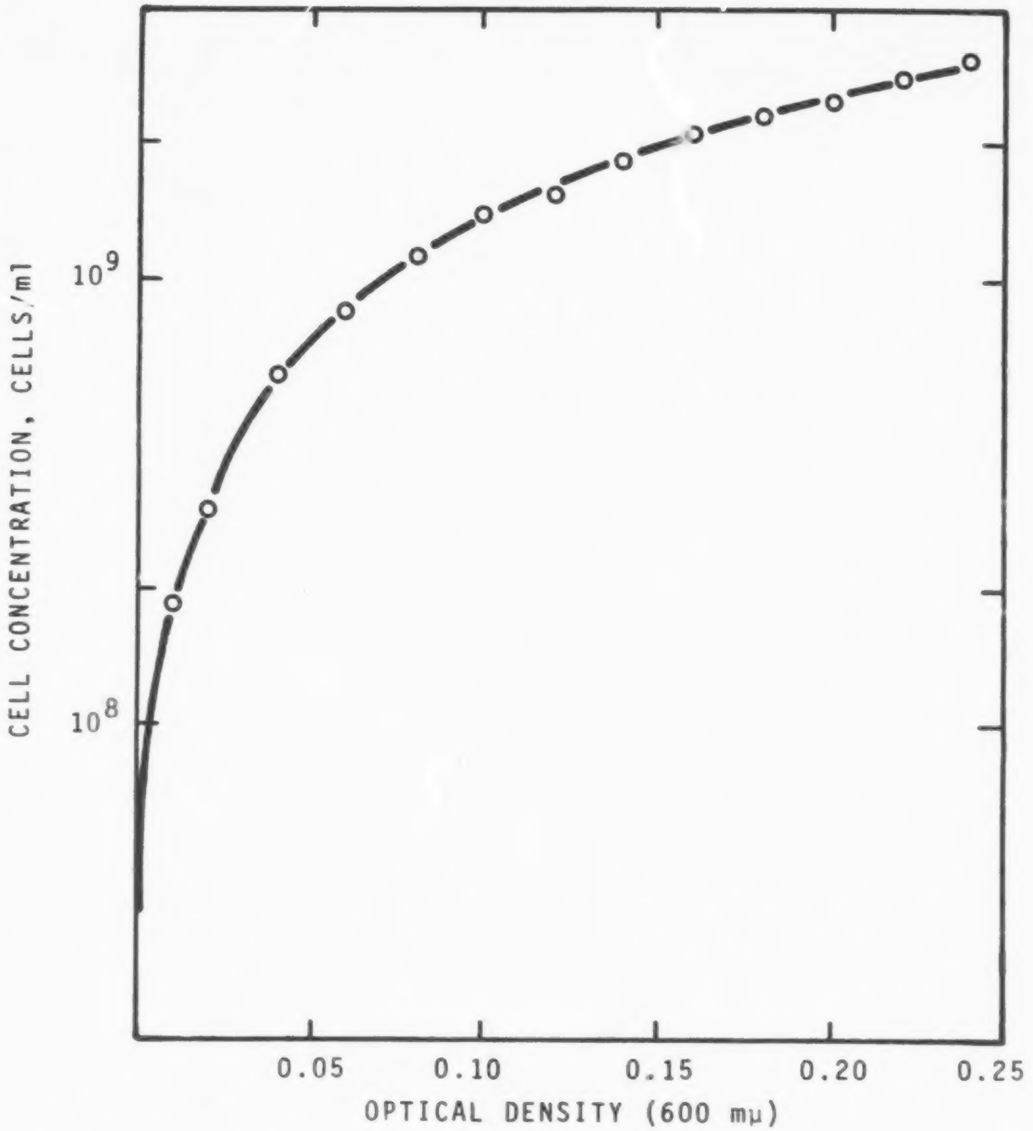

FIGURE 12. ALGAL CELL CONCENTRATION (TENTATIVE COULTER COUNTS) AS A FUNCTION OF SOLUTION OPTICAL DENSITY.

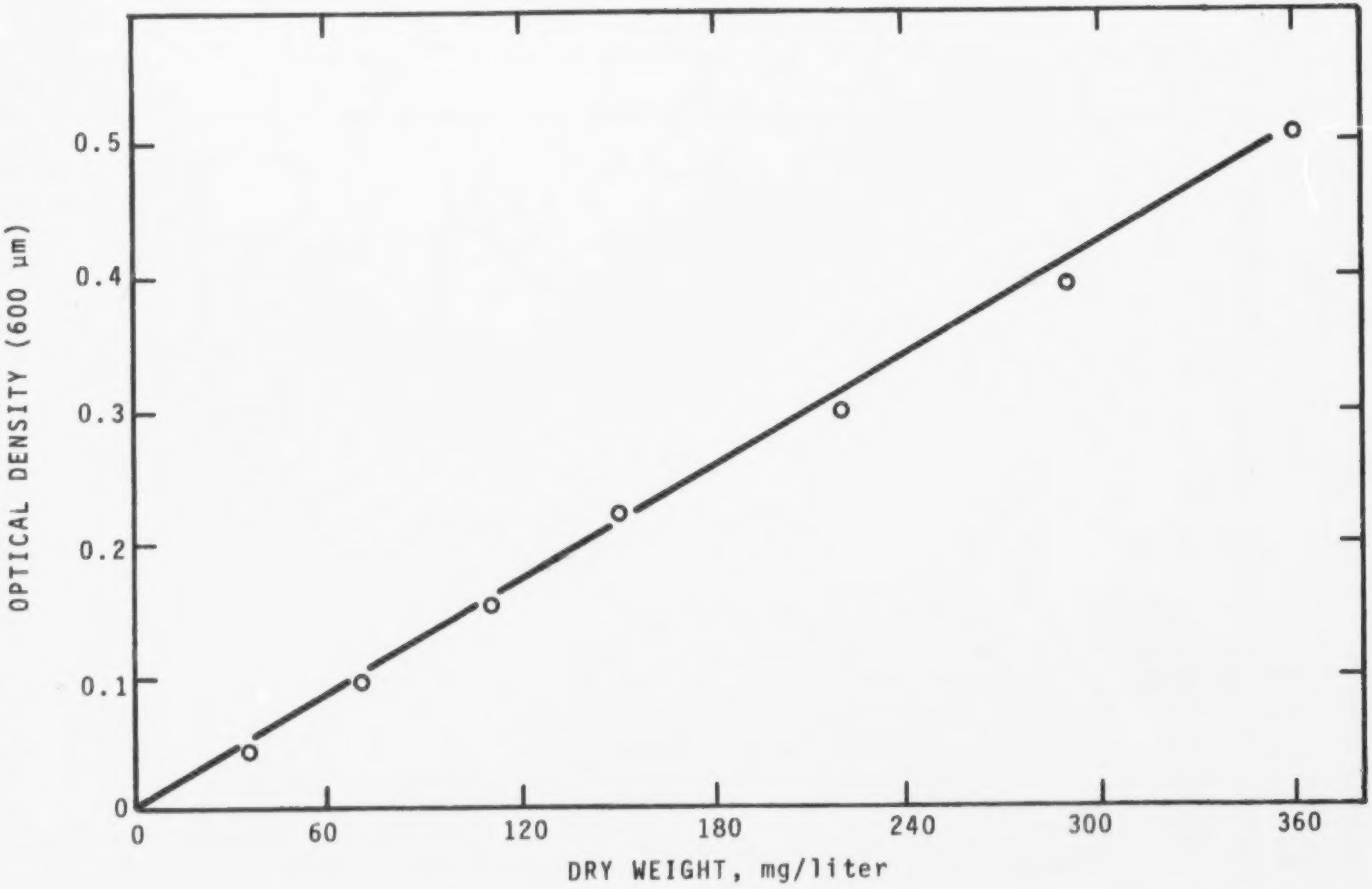

FIGURE 13. SOLUTION OPTICAL DENSITY AS A FUNCTION OF ALGAL DRY WEIGHT.

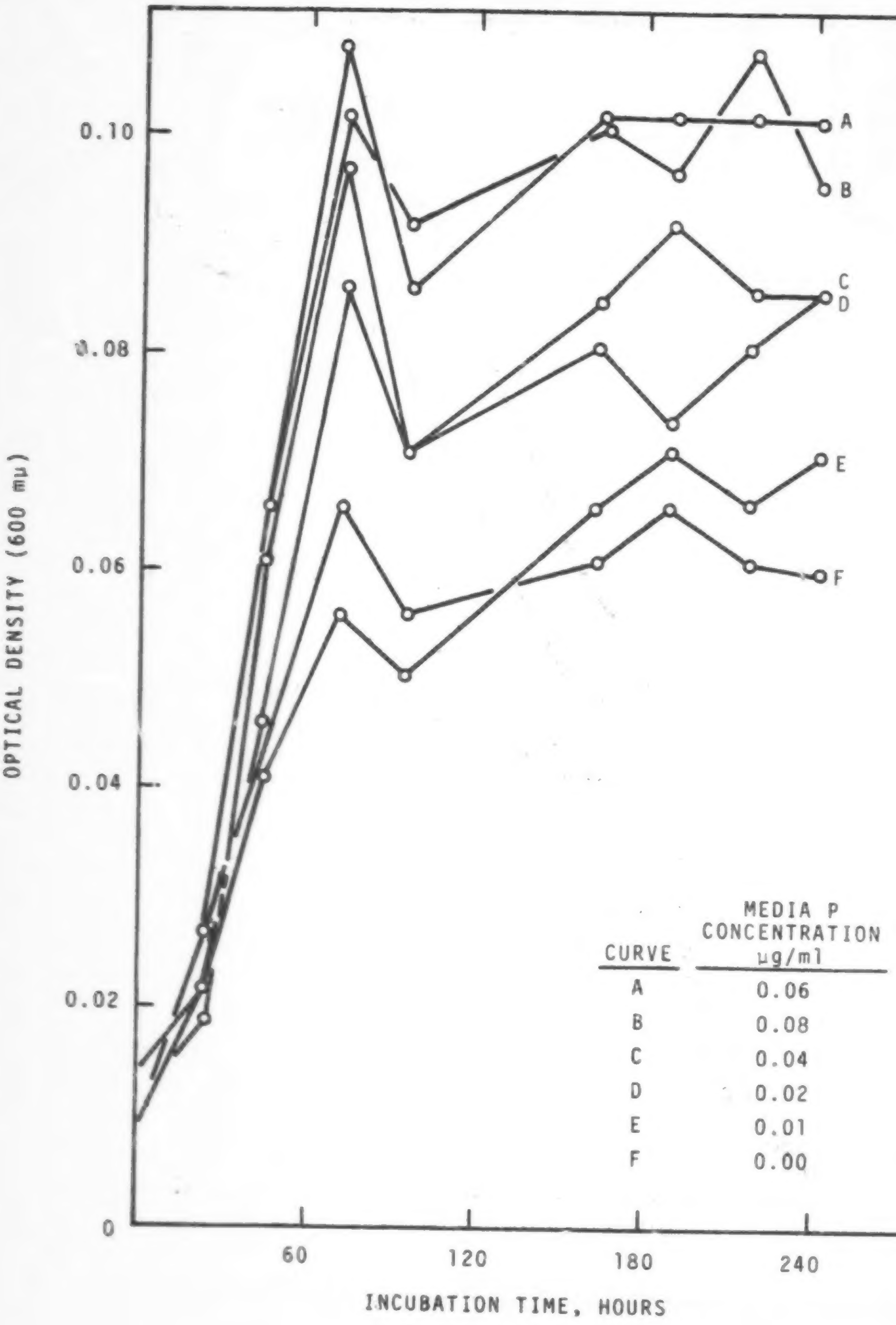

FIGURE 14. STANDARD BIOASSAY GROWTH CURVES (0.00 TO 0.08 μg PHOSPHORUS/ml OF CULTURE MEDIA).

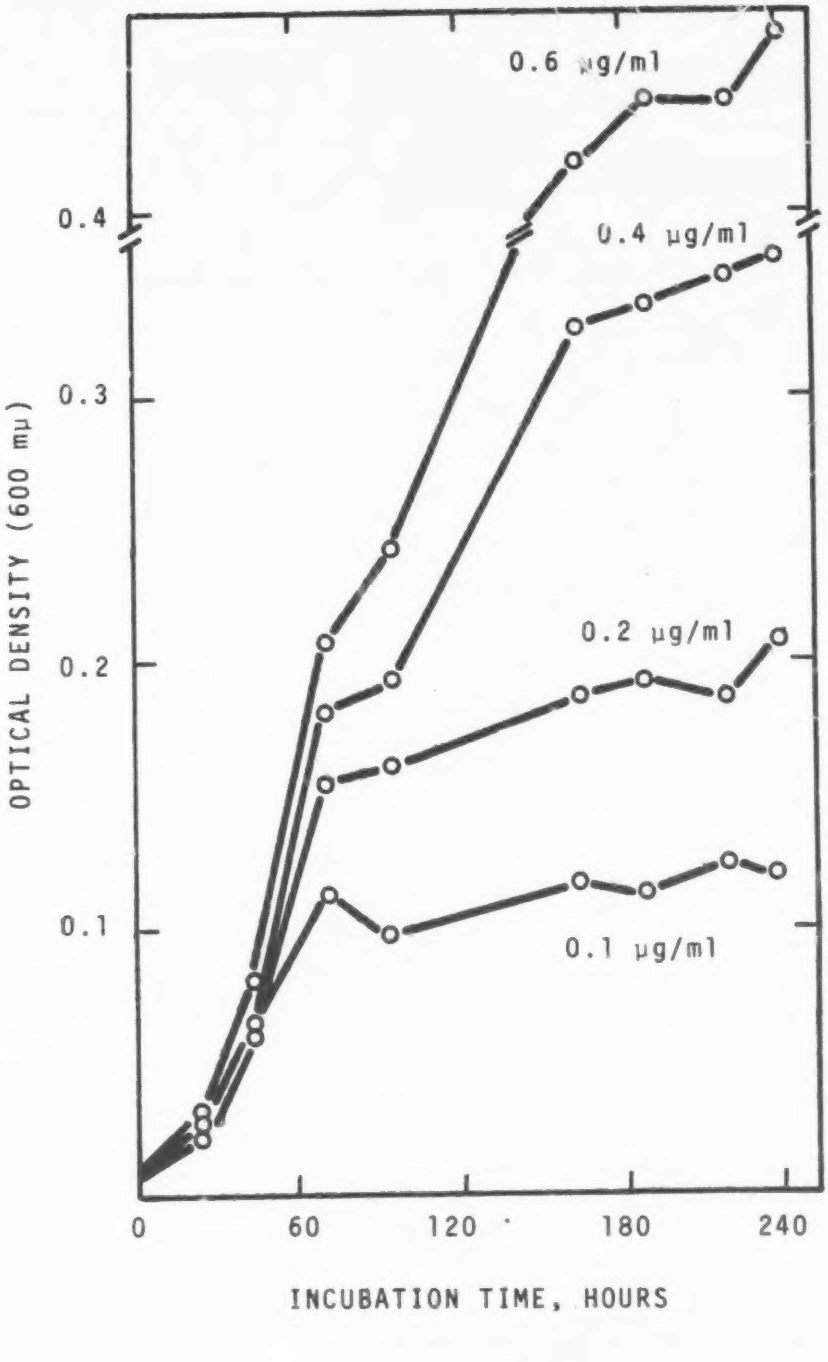

FIGURE 15. STANDARD BIOASSAY GROWTH CURVES (0.1 TO 0.6 µg PHOSPHORUS/ml OF CULTURE MEDIA).

the extent of biomass measured. The relative growth rate increased with decreased biomass. Maximum cell counts were proportional to P concentrations (Figure 16), and these data will be utilized in interpretations, although for comparative purposes, both μ_{max} and maximum cell concentrations will be reported.

B. FACTORS INFLUENCING THE RELEASE AND ALGAL GROWTH POTENTIAL OF SEDIMENT PHOSPHORUS

Studies of the Upper Klamath Lake sediments in the field (Section IV) indicated that changes in the inorganic P fraction were primarily responsible for changes in sediment P status. These changes were negatively correlated as to changes in surface water organic C and, at the Howard Bay location, to surface water temperature. Thus, in the laboratory studies emphasis was placed on the effects of a P sink in the form of an anion exchange resin and algal growth and on temperature as these may have effected changes in sediment inorganic P. In conjunction with the development of methods for measurement of P release and to provide a basis for a broader application of the results of these studies, the influence of sediment and water chemical and physical characteristics and water composition on P release were also evaluated. Where feasible the results of all release studies were related to algal growth potential.

Sediment Physical Parameters and Temperature

This experiment was designed as an initial test, using a cellulose acetate membrane dialysis system, to bracket the influence of sediment:interstital water ratio, sediment:external water ratio and temperature on P release to solution from Upper Klamath Lake sediments.

Materials and Methods

A preliminary study (Table 21) was undertaken to test the membrane dialysis system and to evaluate the influence of the above mentioned parameters on P release to solution utilizing Howard Bay sediments. Experimental details are given in Table 22.

Moist sediment samples were sealed in cellulose acetate dialysis tubing, immersed in distilled water, incubated at 10 C or 23 C, and sampled as previously described in Section V, A.

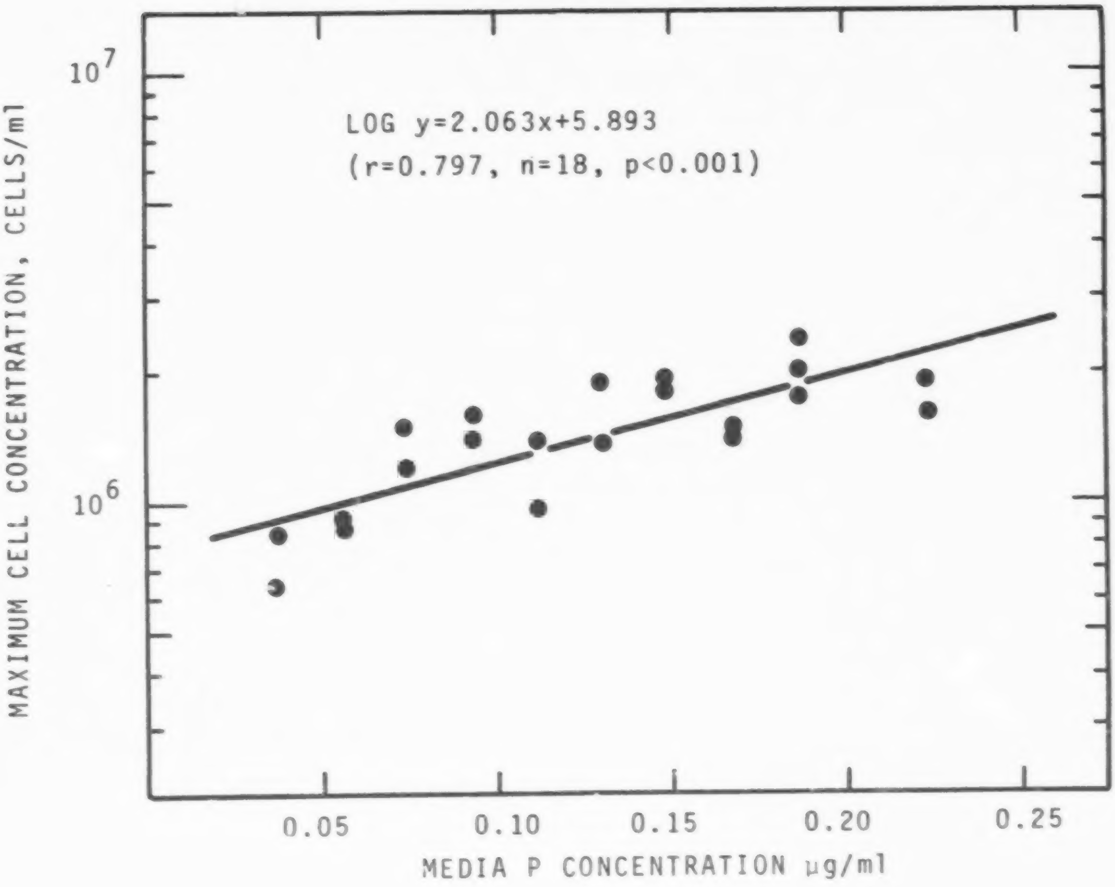

FIGURE 16. STANDARD CURVE OF GROWTH RESPONSE (LOG SCALE) WITH INCREASING LEVELS OF PHOSPHORUS UTILIZING THE REVISED ALGAL BIOASSAY PROCEDURE.

Table 21. Factorial design employed in investigations of phosphorus release to solution (membrane dialysis system).

Independent variable Number	Description	-	+
1	sediment:external water ratio	1:10	1:20
2	sediment:interstitial water ratio	1:5	1:10
3	Temperature	10 C	25 C

Treatment Number	Treatment design for independent variable numbers 1	2	3
1*	-	-	-
2	+	-	-
3*	-	+	-
4	-	-	+
5*	+	+	+
6	-	+	+
7*	+	-	+
8	+	+	-

*duplicated

Table 22. Quantities of sediment and water employed to obtain experimental parameters[1] in phosphorus release studies (membrane dialysis system).

Treatment Number	Sediment	Interstitial[3] Water	Sediment: Interstitial Water Ratio	External[4] Water	Sediment: External Water Ratio
	g	ml		ml	
1a	18.4	101	5.5	184	10.0
1b	19.5	102	5.2	195	10.0
2	19.1	104	5.5	382	20.0
3a	19.9	208	10.4	219	11.0
3b	20.8	208	10.0	208	10.0
4	18.7	102	5.5	186	10.0
5a	17.9	179	10.0	358	20.0
5b	20.8	208	10.0	416	20.0
6	19.3	193	10.0	193	10.0
7a	18.0	95	5.3	326	18.1
7b	20.1	107	5.3	402	20.0
8	19.0	190	10.0	380	20.0

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[1] Table 21

[2] Oven dry (60 C)weight

[3] Lake Water

[4] Distilled water

The total and inorganic P contents of water external to the sediment were measured at periodic intervals.

Results and Discussion

The results of the P release studies are reported for 21-day incubation periods. Limitation of incubation time to 21 days for several treatments was necessitated by the microbial decomposition of the cellulose acetate membrane. To overcome problems of membrane pore size, an alternative to the cellulose acetate membrane in dialysis studies was designed. The new apparatus will be discussed in subsequent sections.

In the P release studies using the cellulose membrane, the pH of the systems remained relatively constant throughout the incubation periods ranging from pH 6.0 to 6.9 for all treatments except for a temporary reduction of approximately 1 pH unit from 2 to 4 days of incubation in Treatments 4 and 5. During this period P was rapidly released from the sediments. The P release continued at an accelerated rate to 10 days of incubation although pH returned to initial levels.

The concentrations of P in the external water during the entire period of incubation are shown in Figures 17, 18, 19, and 20. The influences of the incubation parameters of temperature, sediment:interstitial water ratio and sediment:external water ratio are presented in Tables 23, 24 and 25 respectively, which give the summation of treatment effects for total P in the external water. The results may be summarized as follows: (*i*) both inorganic and organic P were present in the non-sterile external solution within 24 hours of incubation, (*ii*) P release at 10 C was less than 30% of that released at 23 C, (*iii*) maximum P release occurred in systems in which the external water:interstitial water ratio was 2:1 as compared to 1:1 or 4:1, (*iv*) under optimum conditions, P release amounted to several times the quantity of readily exchangeable (NH_4Cl) P.

The limiting pore diameter of the permeable membrane was 25-40 Å precluding the diffusion of microbial cells and suggesting that organic P present in the external water during the initial 1-2 days of incubation diffused from the sediment as it is unlikely that significant microfloral populations developed in the water during this period. After approximately 15 days, the membrane was observed to be decomposing, therefore, the extent of degradation of the membrane during incubation is unknown and limiting pore diameter after the initial phases

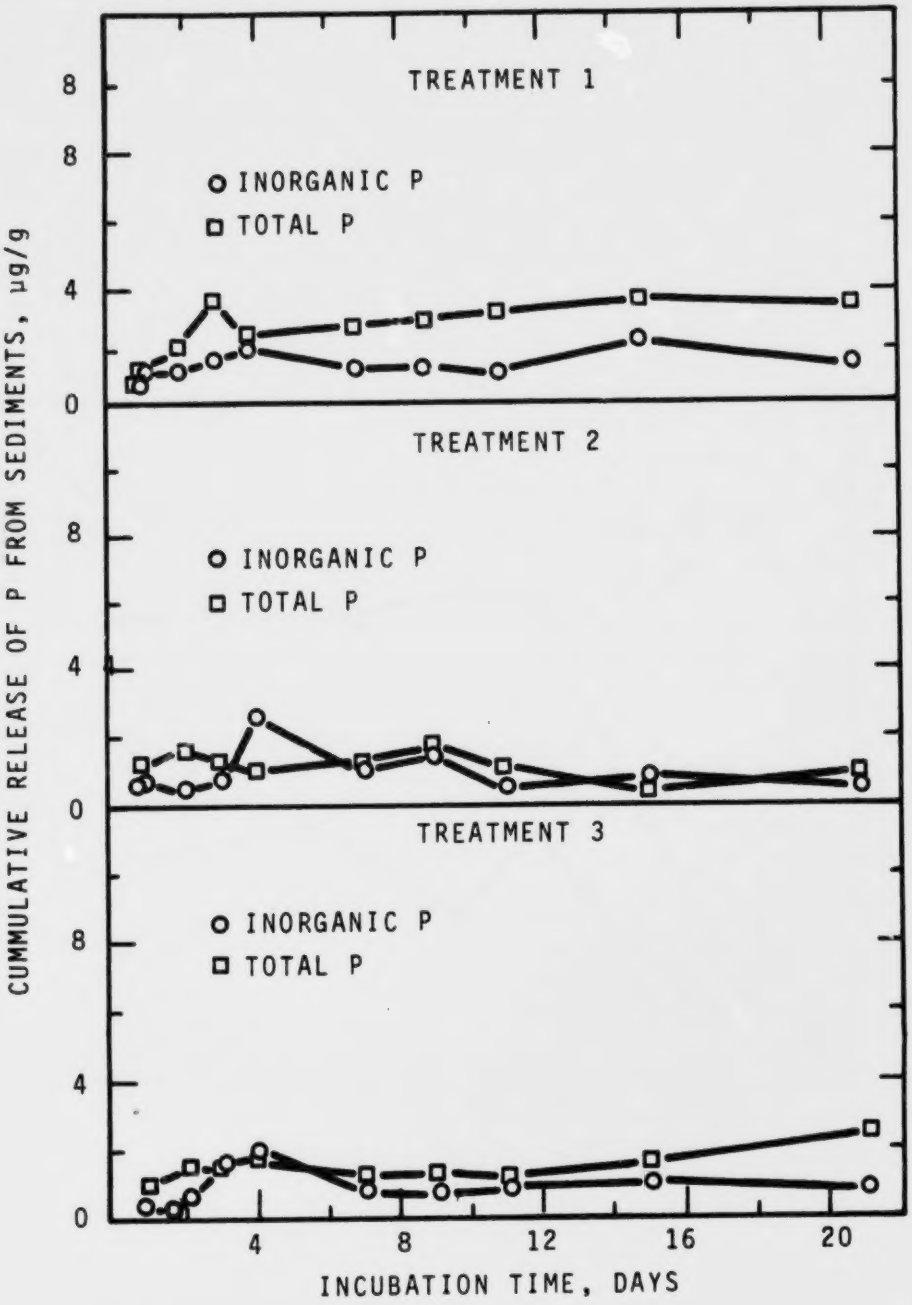

FIGURE 17. CONCENTRATION OF TOTAL AND INORGANIC PHOSPHORUS IN THE EXTERNAL WATER DURING INCUBATION OF LAKE SEDIMENTS (MEMBRANE DIALYSIS SYSTEM) OVER A RANGE OF EXPERIMENTAL PARAMETERS (TREATMENTS 1,2,3; TABLE 21).

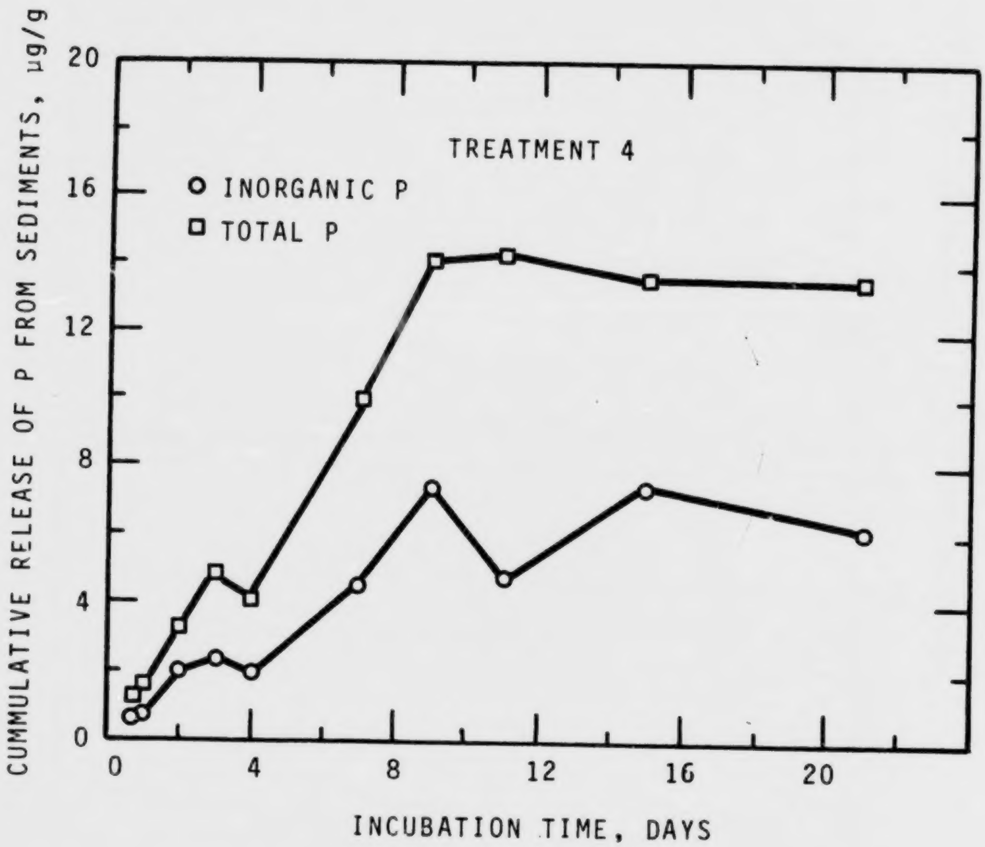

FIGURE 18. CONCENTRATION OF TOTAL AND INORGANIC PHOSPHORUS IN THE EXTERNAL WATER DURING THE INCUBATION OF LAKE SEDIMENTS (MEMBRANE DIALYSIS SYSTEM) OVER A RANGE OF EXPERIMENTAL PARAMETERS (TREATMENT 4, TABLE 21).

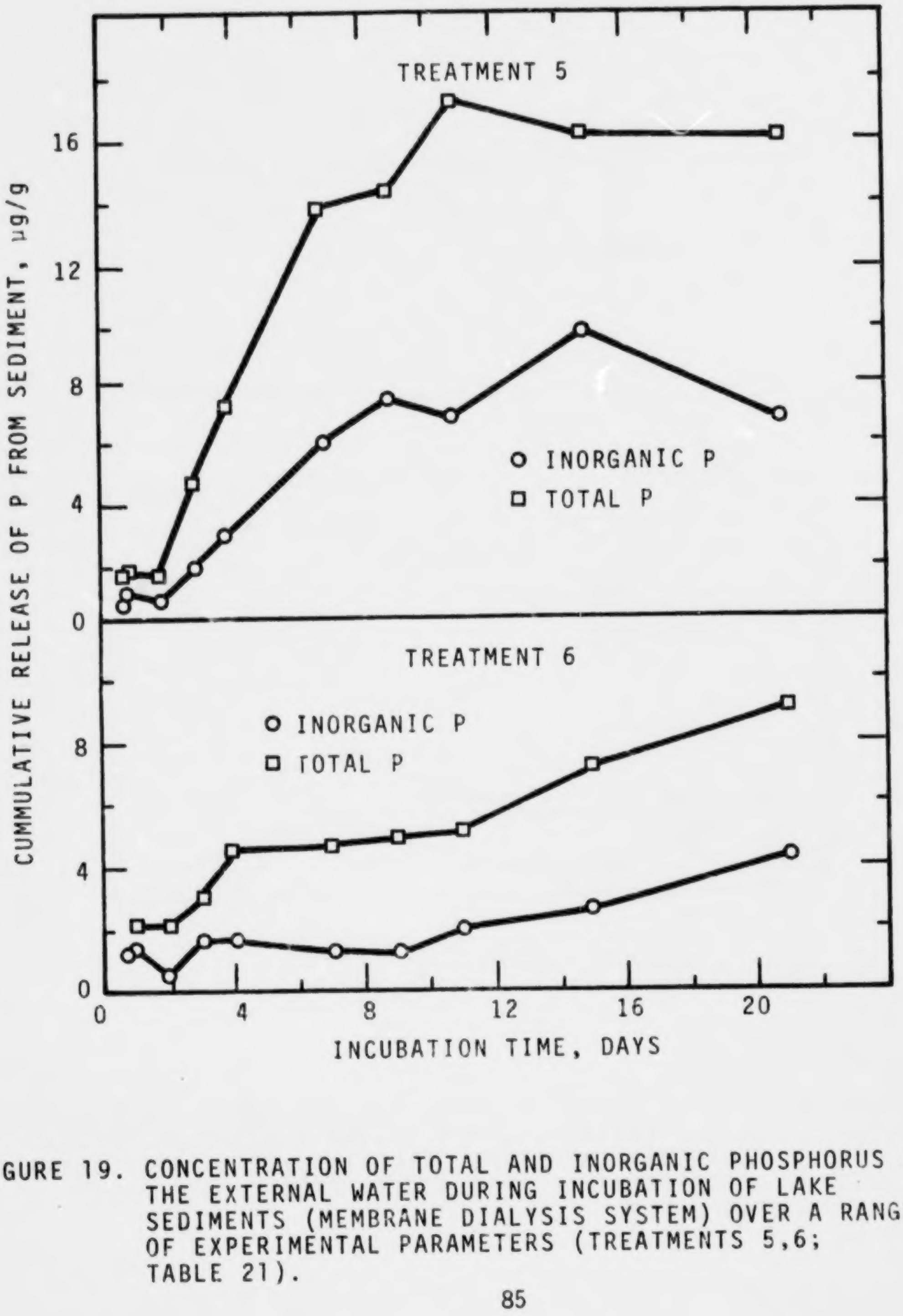

FIGURE 19. CONCENTRATION OF TOTAL AND INORGANIC PHOSPHORUS IN THE EXTERNAL WATER DURING INCUBATION OF LAKE SEDIMENTS (MEMBRANE DIALYSIS SYSTEM) OVER A RANGE OF EXPERIMENTAL PARAMETERS (TREATMENTS 5,6; TABLE 21).

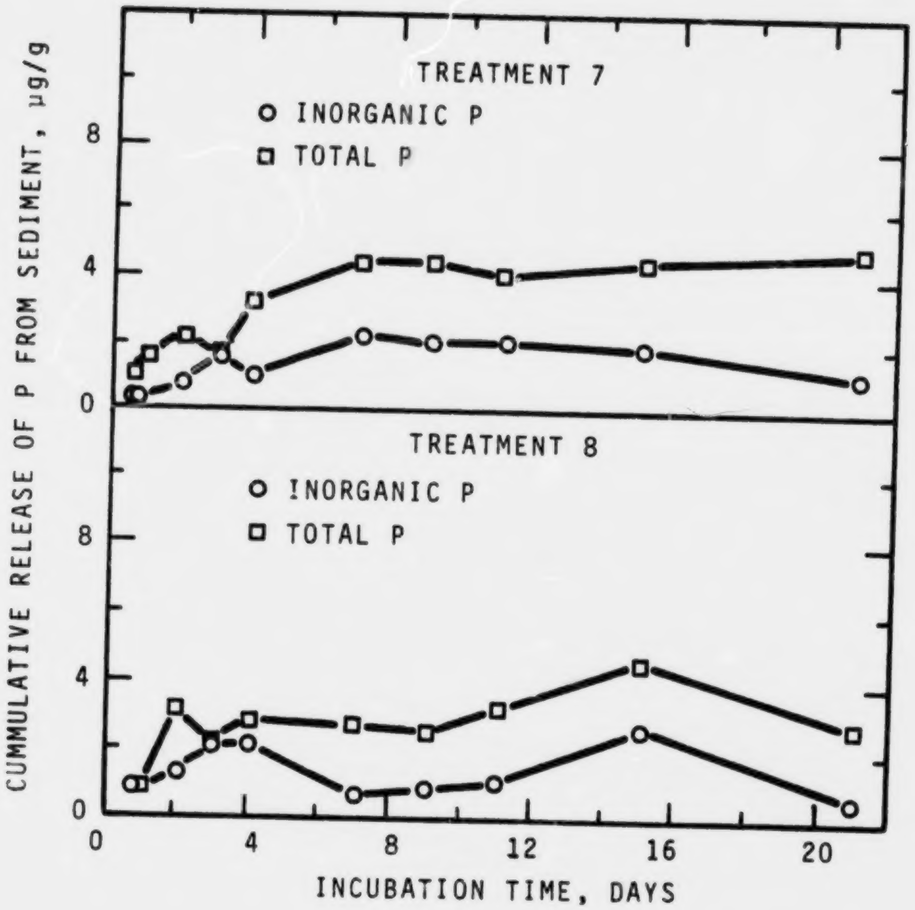

FIGURE 20. CONCENTRATION OF TOTAL AND INORGANIC PHOSPHORUS IN THE EXTERNAL WATER DURING INCUBATION OF LAKE SEDIMENTS (MEMBRANE DIALYSIS SYSTEM) OVER A RANGE OF EXPERIMENTAL PARAMETERS (TREATMENTS 7, 8; TABLE 21).

of incubation can not be precisely defined.

Sediment Chemical Composition and Temperature

Investigations were designed to (*i*) measure the rate and extent of P release to solution as a function of sediment composition and temperature, (*ii*) develop a multiple regression model, incorporating variables selected on the basis of (*i*) above, for the prediction of the extent of P release at given time intervals and (*iii*) estimate the algal growth potential of released P utilizing the EPA Provisional Bioassay.

Materials and Methods

P release from moist Upper Klamath and Agency Lake sediment samples was determined using the filter dialysis system. The filter dialysis system was designed as an alternative to the cellulose membrane dialysis system and has been previously described (Section V, A).

For the release experiment, the sediments (Table 26), partitioned from distilled water by a 0.45 μ filter, were incubated in the dark at 10 C and 23 C for a period of 45 days and total and inorganic P released to the external water were measured at periodic intervals.

To determine sediment and experimental parameters influencing the rate and extent of P release to solution, a multiple regression analysis of the experimental results was undertaken. The following variables were considered for their relative influence on 9, 16 and 31 day cummulative P release values: (*i*) sample weight (g), (*ii*) weight of sediment (g), (*iii*) water volume in water cell (ml), (*iv*) water volume in sediment cell (ml), (*v*) total P (μg/g), (*vi*) inorganic P (μg/g), (*vii*) organic P (μg/g, %), (*viii*) temperature (C), (*ix*) sediment solids (g/100 ml), (*x*) ratio of water volume in sediment cell to volume in water cell, (*xi*) interactions, i.e. temperature and organic P and temperature and inorganic P. After considering possible combinations of these variables on the computer, a model was selected which best described or predicted P release at given time intervals.

The algae Selenastrum capricornutum was employed as previously described (Section V, A) to assay the availability of P released to solution from sediments.

To test the bioassay method, dialysis cell solutions from Treatments 1 through 4 (Table 26) were employed. The solutions

Table 23. Influence of incubation temperature on phosphorus release from sediments (membrane dialysis system).

Comparable treatment[1]	Summation of external water P contents[2,3] at		
	10 C (A)	23 C (B)	$\frac{A}{B}$
	----------------μg P/g sediment------------		
1a	41.8		0.40
1b	22.6		
4		80.0	
2	10.0		0.32
7a		43.0	
7b		20.1	
3a	13.9		0.33
3b	15.2		
6		44.2	
5a		117	0.27
5b		71.0	
8	25.2		

---

[1] Table 21

[2] Total P measurement; 21 days of incubation

[3] Duplicates averaged

Table 24. Influence of sediment: interstitial water ratio on phosphorus release from sediments (membrane dialysis system).

Comparable treatment[1]	Summation of external water P contents[2,3] at sediment:interstitial water ratios of 1:10 (A)	1:5 (B)	$\frac{A}{B}$
	-----------------	µg P/g sediment	-------
1a		41.8	
1b		22.6	
3a	13.9		0.45
3b	15.2		
2		10.0	2.52
8	25.2		
4		80.0	0.55
6	44.2		
5a	117		
5b	71.0		
7a		43.0	2.98
7b		20.1	

---

[1] Table 21

[2] Total P measurement; 21 days of incubation

[3] Duplicates averaged

Table 26. Experimental design employed in investigations of the influence of temperature and lake sediment composition on phosphorus release to solution.

Temperature	Sediment sample designation[1]	Sediment composition					Treatment number
		Wet weight	Total solids	Total P	Inorganic P	Organic P	
C		g	%	-----µg/g------------			
10	H-2	322	7.7	417	200	271	1a
23	H-2	244	7.7	417	200	271	1b
10	A	383	13.7	709	449	260	2a
23	A	340	13.7	709	449	260	2b
10	H-4	372	8.1	823	441	382	3a
23	H-4	336	8.1	823	441	382	3b
10	P-4	246	9.2	507	247	260	4a
23	P-4	315	9.2	507	247	260	4b

[1] Table 1, A represents Agency Lake

were removed after 45 days of incubation. The P concentrations of the solutions utilized are given in Table 27. The solutions were assayed directly by inoculation with the test organism and measurement of its growth rate without further addition of nutrients.

Results and Discussion

The quantities of total P, inorganic P and organic P released to solution during incubation of lake sediments at 10 and 23 C are illustrated in Figure 21 and 22. In general, the rate of P release to solution increased with time. Inorganic P generally constituted the major portion of P released to 31 days of incubation. However, at 45 days of incubation, the contribution of organic P to total P had increased amounting to 30-80% of the total P detected. Temperature had a marked effect on P release to solution, with the maximum P release occurring at the high temperature level. After 45 days of incubation, organic P constituted a larger fraction of total P at the low temperature values. Relatively large quantitites of P were released from sediment H-4 (Treatments 3a and b) at both temperature levels. Sediment H-4 contained higher concentrations of total P and organic P than the other sediments investigated.

Multiple correlation, based on the data described in Tables 26 and 27, was employed to develop a model for the description of P release in these systems. Consideration of the possible sediment and experimental parameters influencing release using computer simulation techniques resulted in the selection of several influential variables which were incorporated into the following model:

$$Y = B_0 + B_1X_1 + B_2X_4 + B_3(X_1 \cdot X_4) + B_4X_5$$

where Y = total solution P at 16 or 31 days of incubation

B_0, B_1, B_2, B_3, and B_4 = partial regression coefficients

X_1 = incubation temperature

X_4 = organic phosphorus (μg/100 g)

X_5 = total solids (g/100 ml)

$X_1 \cdot X_4$ = temperature, organic phosphorus interaction

Table 27. Concentrations of total phosphorus and inorganic phosphorus in the external water after incubation of sediments for 45 days in a dialysis cell.

Treatment Number[1]	Concentration in solution of Total P	Inorganic P
	----------------μg/ml	-------------------------
1a	0.23	0.14
1b	0.64	0.35
2a	0.01	0.00
2b	0.45	0.17
3a	1.66	1.00
3b	6.08	3.87
4a	0.19	0.08
4b	0.58	0.30

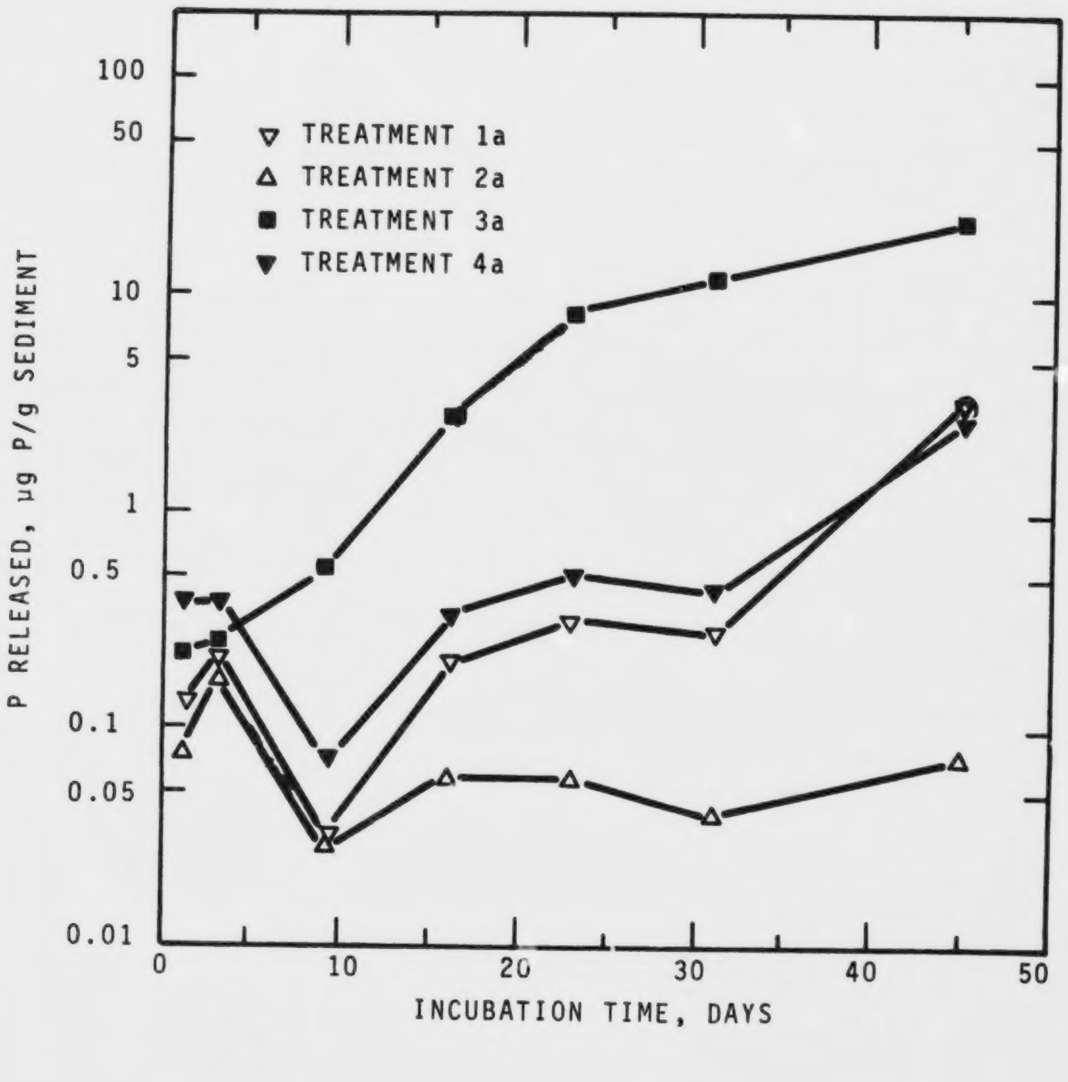

FIGURE 21. CONCENTRATION OF TOTAL SOLUTION PHOSPHORUS IN THE EXTERNAL WATER DURING INCUBATION AT 10 C OF UPPER KLAMATH AND AGENCY LAKE SEDIMENTS IN A DIALYSIS CELL.

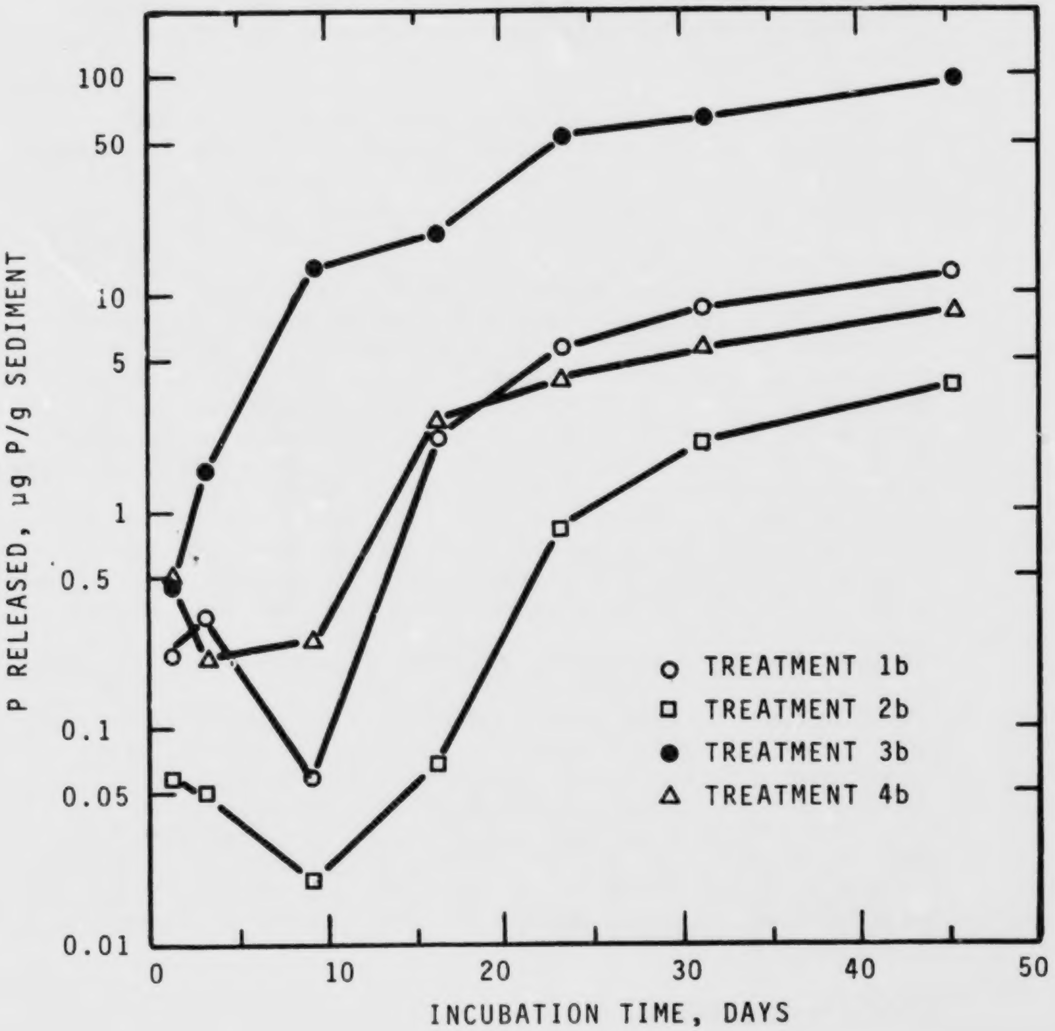

FIGURE 22. CONCENTRATION OF TOTAL SOLUTION PHOSPHORUS IN THE EXTERNAL WATER DURING INCUBATION AT 23 C OF UPPER KLAMATH AND AGENCY LAKE SEDIMENTS IN A DIALYSIS CELL.

The ability of the model to predict P release to solution in the dialysis systems after 16 and 31 days incubation is outlined in Table 28. At both time intervals the multiple regression coefficient and residual variance values indicated excellent correlation with good predictive capability and low inherent variance.

Of the solutions subjected to bioassay (Table 27), growth of the test organism occurred only in solutions from Treatments 3a and b (Figure 23) which contained 1.00 and 3.87 μg P/ml. Treatments 3a and b exhibited optical densities of 0.237 and 0.222 respectively after 436 hr of incubation corresponding to an inorganic P solution concentration, determined from total growth in the bioassay method, of approximately 0.25 μg/ml (Figure 15). The growth rate of organisms in solutions from Treatments 3a and b was slower with growth approaching the stationary phases after approximately 240 hours of incubation compared to solutions containing a complete nutrient supply (Figure 14, 15) which generally attained the stationary phase at 60 to 150 hours. The solutions were assayed without additional essential nutrients. Available nutrient supplies in the dialysate had to originate from the sediment. The different response of the test organisms in solutions where growth occurred compared to the standard curves (Figure 14, 15) reflects a deficiency of nutrients other than P which was not limiting.

Sediment Inorganic Phosphorus Equilibria and Long-Term Incubation

The objectives of this investigation were to determine (*i*) the rate and extent of P release from sediments in the dialysis system over a 90 day incubation period, (*ii*) changes in sediment mineral components which occurred on incubation (*iii*) the extent of sediment sorption of ^{32}P spiked into the water half-cell, i.e. the equilibrium distribution of P during release, (*iv*) the sediment mineral component into which the sorbed ^{32}P was incorporated and (*v*) the algal growth potential of released P.

Materials and Methods

Sediments taken in April, 1971, from the Howard Bay, Buck Island and Pelican Marina locations on Upper Klamath Lake were incubated in the dark at 25 C in a dialysis system containing distilled water or a dilute P solution. In the present studies, the dialysis cells were gently shaken as opposed to the static systems employed previously. In addition to distilled water treatments, replicate water half-cells were spiked with a

Table 28. Prediction, using a multiple regression model, of the influence of temperature and lake sediment composition on the release of sediment phosphorus to solution.

Treatment number	Total P release to solution Observed	 Predicted
	------------- µg/g	----------------
	After 16 days incubation	
1a	0.20	0.58
1b	2.15	3.04
2a	0.06	-0.21
2b	0.07	0.75
3a	2.23	2.20
3b	19.77	19.69
4a	0.33	0.26
4b	2.71	1.22
Multiple correlation coefficient	0.986	
Residual variance	1.23	
	After 31 days incubation	
1a	0.29	1.35
1b	8.75	9.52
2a	0.04	-0.53
2b	2.07	3.23
3a	12.53	12.43
3b	65.29	65.22
4a	0.44	0.05
4b	5.66	3.80
Multiple correlation coefficient	0.998	
Residual variance	2.32	

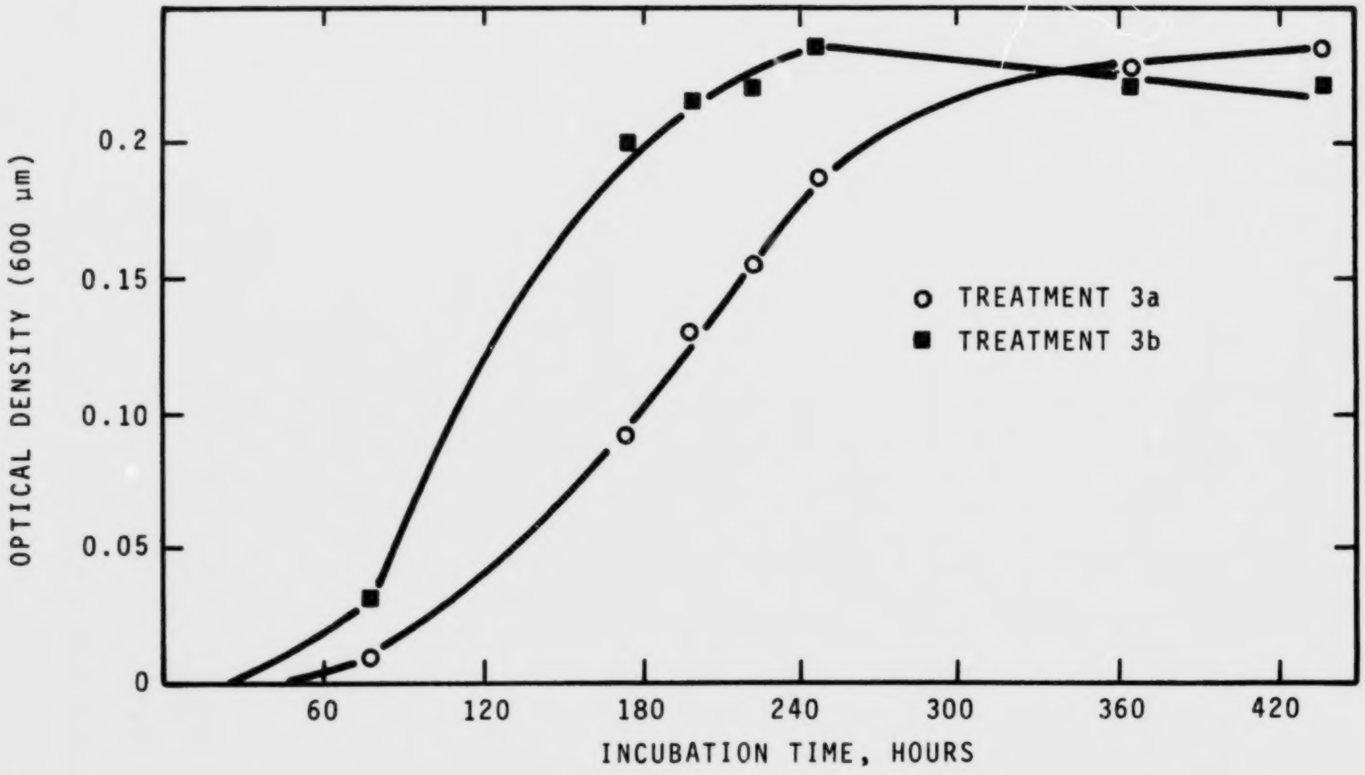

FIGURE 23. ALGAL GROWTH RESPONSE IN DIALYSATES (TABLE 27) OF LAKE SEDIMENTS.

solution containing 1 ppm P as KH_2PO_4 and ^{32}P to determine if resorption occurred. The experimental design is outlined in Table 29. Dialysates from Treatments 1, 2, 3, and 7 were analyzed periodically for pH, total and inorganic P. Up to 41 days of incubation, aliquots of the solution were removed for analysis. After 41 days the dialysates were drained completely and the cells refilled with water. This procedure was continued in all subsequent experiments. Dialysates from Treatments 4, 5, 6, and 8 were analyzed at the end of a 30 day incubation period for total P and ^{32}P in solution.

Sediment interstitial waters were separated by gravity filtration over a Whatman Number 40 filter paper. To remove suspended solids, the filtrate was passed through a 0.45 μ filter. Separated interstitial waters were subsequently analyzed for total and inorganic P.

The sediments not receiving the ^{32}P spike (Treatments 1, 2, 3, and 7; Table 29) were analyzed at the end of a 90 day incubation period for total, inorganic and organic P and for the distribution of P in P mineral fractions. Sediments equilibrated with ^{32}P (Treatments 4, 5, 6 and 8; Table 29) were analyzed in a similar manner at the end of the 30 day incubation period except that the sediment P mineral extracts were also analyzed for ^{32}P.

The determination of ^{32}P in sediment fusion extracts, acid extracts of inorganic P, and P fractionation extracts was accomplished using a liquid scintillation cocktail consisting of an aqueous mixture of approximately 460 g/ℓ toluene, 230 g/ℓ Triton X-100, 4 g/ℓ POPOP and 11 g/ℓ $Ca(OH)_2$.

An aliquot (1 ml) of each solution to be counted was pipetted into a scintillation vial. A second aliquot (10 ml) of scintillation cocktail and sufficient distilled water to bring to volume (20 ml) were added. All counting was related to the ^{32}P content of the initial solution added to the water dialysis cells. Standards for each extract were prepared by pipetting a standard ^{32}P solution (1 ml) and an analogous extract (1 ml) containing no ^{32}P into a scintillation vial and adding scintillation cocktail and distilled H_2O. Blanks for background were similarly prepared, omitting the ^{32}P solution.

To assay the growth potential of the nutrients released by the sediments, dialysate solutions from Treatments 1, 2, 3 and 7 (Table 29) sampled after 41 days of incubation, were inoculated with the algae Selenastrum capricornutum and incubated as

Table 29. Experimental design employed in investigations of sediment phosphorus release to solution.

Treatment number	Sediment sample designation[1]	Sediment Composition				Initial water P content[2]
		Wet weight	Total solids	Total P	Inorganic P	
		g	%	-----µg/g----------		µg/ml
1	H-13	481	9.1	1033	574	0.0
2	B-13	492	9.1	629	295	0.0
3	P-15	480	10.2	662	348	0.0
4	H-13	469	9.1	1033	574	1.0
5	B-13	478	9.1	629	295	1.0
6	P-15	457	10.2	662	348	1.0
7	H-13	456	9.1	1033	574	0.0
8	H-13	438	9.1	1033	574	1.0

---

[1] Table 1

[2] Water cells amended with P also contain P^{32} spike

described by National Eutrophication Research Program (1971). This revised version of the method described in Section V, A was utilized for bioassays in all subsequent experiments. In addition to direct measurements on the dialysates, aliquots of the dialysates spiked into the recommended growth media were also evaluated to determine standard growth potential. Algal biomass was estimated by direct microscopic counting (Neubauer counting chamber).

Results and Discussion

The sediment interstitial water compositions prior to dialysis are given in Table 30. The Howard Bay sediment which exhibited highest total P values contained 66.0 µg total P/g of sediment in the interstitial water whereas interstitial waters of Buck Island and Pelican Marina sediments contained less than 1.0 µg P/g of sediment.

The results of long-term dialysis of Upper Klamath Lake sediments are summarized in Tables 31-33. Linear regressions describing sediment release are illustrated in Figure 24.

Differences in the rate and extent of P release in the dialysis systems reflected differences in total sediment P (Table 29) and interstitial water P concentration. After 30 days of dialysis, the Howard Bay, Buck Island and Pelican Marina sediments had released P amounting to 45.8, 8.4 and 9.9 µg P/g of sediment, respectively. Howard Bay sediments, containing high concentrations of P in the interstitial waters relative to the other sediments, released greater quantities of P to solution, and total P released was less than that present in the interstitial waters. However, the Buck Island and Pelican Marina sediments released at least a factor of 8 or more P to solution than was present in the interstitial waters indicating that P was released from the solid phase. Inorganic P accounted for most of the P present in the water cell. After 90 days of incubation, the release rate was nearly constant or had decreased and total P release amounted to 143.0, 39.9 and 40.7 µg P/g for sediments of Howard Bay, Buck Island, and Pelican Marina, respectively. Thus, as after 30 days incubation, maximum total release occurred in Howard Bay sediments, however, this amounted to only approximately 2 times the quantity originally present in the interstitial waters. P release from the other sediments was a factor of at least 40 greater than that present in the interstitial waters, and thereby originated primarily from the solid phase. Over 95% of the P in the external water was inorganic P. Thus, soluble

Table 30. Sediment interstitial water composition prior to dialysis.

Sediment samples	Interstitial water total P content	
	µg/ml	µg/g[1]
Howard Bay	6	66.0
Buck Island	<0.1	<1.0
Pelican Marina	<0.1	<1.0

---

[1] Based on oven dry (60 C) weight

Table 31. Concentrations of total phosphorus and inorganic phosphorus in the external water during incubation of replicate Howard Bay sediments in dialysis cells (Treatments 1 and 7).[1]

Incubation time	pH Treatment 1	pH Treatment 7	Total P Treatment 1	Total P Treatment 7	Inorganic P Treatment 1	Inorganic P Treatment 7
			------μg P/g sediment			----------
3	6.4	6.3	1.2	2.4	1.3	2.1
6	6.3	6.3	5.9	5.9	3.7	5.8
9	6.5	6.5	10.6	13.2	7.9	12.5
13	6.6	6.7	15.4	17.5	14.6	17.5
16	6.6	6.7	20.2	21.5	19.3	21.1
20	6.6	6.6	28.0	29.4	27.0	27.6
23	6.7	6.7	35.1	33.2	33.5	31.7
27	6.6	6.6	42.0	37.8	39.8	36.7
30	6.5	6.5	45.8	42.9	44.4	41.1
41	6.9	6.9	64.1	62.7	61.5	58.4
57	6.7	6.6	94.9	93.5	92.1	89.2
66	6.5	6.4	112.4	112.5	109.1	108.0
90	6.5	6.5	143.0	148.8	138.9	144.5

---

[1] Table 29

Table 32. Concentrations of total phosphorus and inorganic phosphorus in the external water during incubation of Buck Island sediments in a dialysis cell (Treatment 2).[1]

Incubation time	pH	Total P	Inorganic P
days		---------μg P/g sediment -----------	
3	6.3	0.4	<0.1
6	6.1	0.7	0.1
9	6.4	1.6	0.9
13	6.8	2.0	1.7
16	6.6	3.4	3.1
20	6.6	4.9	4.6
23	6.9	5.9	5.5
27	6.6	7.4	6.6
30	6.5	8.4	7.6
41	7.3	12.8	11.5
57	6.7	19.4	17.8
66	6.3	27.0	25.1
90	6.4	39.9	38.0

[1] Table 29

Table 33. Concentrations of total phosphorus and inorganic phosphorus in the external water during incubation of Pelican Marina sediments in a dialysis cell (Treatment 3).[1]

Incubation time	pH	Total P	Inorganic P
days		µg P/g sediment	
3	6.3	<0.1	<0.1
6	6.1	0.4	<0.1
9	6.4	1.5	0.8
13	6.6	2.0	1.8
16	6.5	3.4	2.9
20	6.6	5.6	4.7
23	6.7	6.8	6.2
27	6.6	8.9	7.8
30	6.4	9.9	9.2
41	7.0	14.6	13.1
57	6.5	26.8	25.3
66	6.3	31.4	29.7
90	6.3	40.7	39.1

[1] Table 29

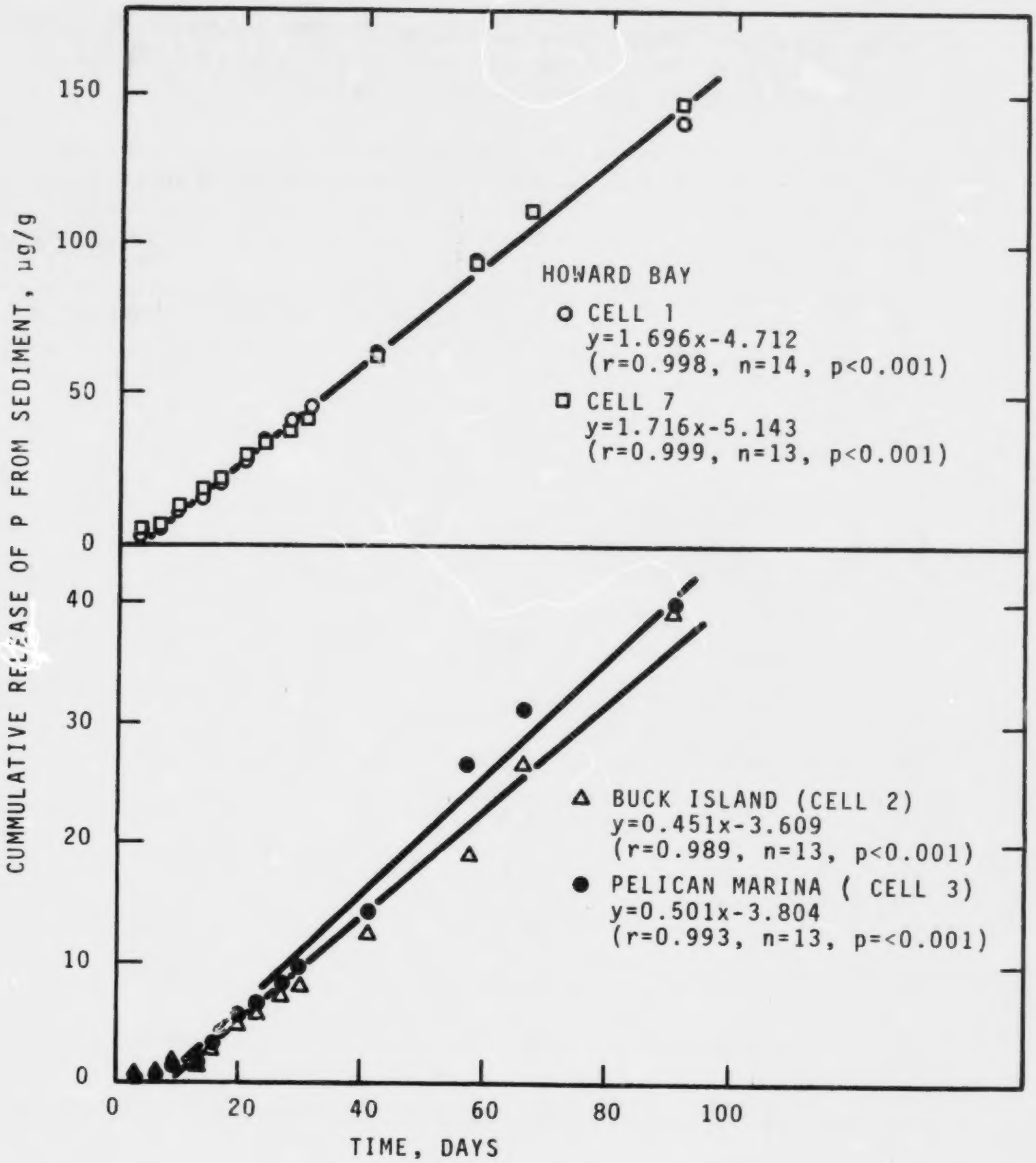

FIGURE 24. SEDIMENT PHOSPHORUS RELEASE AS A FUNCTION OF INCUBATION TIME IN DIALYSIS SYSTEMS(TABLE 29).

organic P compounds were not diffused through the 0.45 μ filter and the external water cell remained largely sterile although aseptic techniques were not employed.

Approximately 6% and 12% of the total and inorganic P fractions of Buck Island and Pelican Marina sediments were released to solution during incubation (Table 34). Larger percentages were released from Howard Bay sediments amounting to approximately 14 and 25% for total and inorganic P, respectively. However, if the P present in the interstitial waters is subtracted (6.1% of total P in the case of Howard Bay sediments; Tables 29, 30) it may be concluded that similar quantities of P were released from the solid phase of sediments from all locations. Thus, whereas more P is available for algal growth at Howard Bay the contribution of the solid phase to release is approximately equivalent to the other locations.

It is noteworthy that Treatments 1 and 7 (Table 29), replicates, were quite comparable during the entire course of the study providing substantiation for the precision of the methods employed.

The relative changes in sediment total P and in P mineral components during long-term incubation in the dialysis system are summarized in Tables 35-37. It should be recognized that procedural errors in the mineral fractionation scheme may bracket relatively small differences in sediment P effected by P release to solution. However, these studies were conducted to establish if trends in mineral P dissolution accompanied release. The following comparisons were undertaken for that purpose.

Sediments from all locations exhibited reductions in total sediment P. In the case of Howard Bay, reductions in total sediment P closely approximated that P released to solution (Table 31). The agreement was not as close for Buck Island and Pelican Marina sediments (Tables 32 and 33) but differences were within procedural error. Changes in inorganic P measured in Treatments 1-8 accounted for most of the reduction in sediment P on incubation for Howard Bay and Buck Island sediments (Table 35 and 36). However, Pelican Marina sediments (Table 37) exhibited an increase in inorganic P measured in this manner. In absolute terms, the readily exchangeable (NH_4Cl) fraction was reduced to less than detectable levels in all cases. Most of the reductions in Howard Bay and Buck Island sediments occurred in the NH_4F and NaOH (0.1 $\underline{M}$) fractions. Pelican Marina sediments exhibited a reduction only in the NaOH (0.1 $\underline{M}$) fraction with other fractions exhibiting increases. In terms of overall

Table 34. Fraction of sediment total and inorganic phosphorus released to the external water during incubation (90 days) of Upper Klamath Lake sediments in dialysis cells.

Treatment[1]	Sediment sample	Concentrations of P in external water			
				Fraction of sediment[1]	
		Total P	Inorganic P	Total P	Inorganic P
		------ µg/g ----------		---------%-------------	
1	Howard Bay	143.0	138.9	13.8	24.2
7	Howard Bay	148.8	144.5	14.4	25.2
2	Buck Island	39.9	38.0	6.3	12.9
3	Pelican Marina	40.7	39.1	6.1	11.2

[1] Table 29

Table 35. Relative changes in total phosphorus and in inorganic phosphorus fractions of Howard Bay sediments on long-term incubation in the dialysis system.

Chemical treatment[1]	Sediment inorganic P		
	Before incubation	After 90 day incubation	Alteration
	µg/g		
1 NH_4Cl	6	1	-5
2 NH_4F	213	148	-65
3 NaOH (0.1M)	142	87	-55
4 $Na_2S_2O_4$-$Na_3C_6H_5O_2$	62	43	-19
5 NaOH (1.0M)	29	87	+58
6 HCl	24	20	-4
7 Ignition	0	0	0
8 Fusion	56	42	-14
Total Treatments 1 8	532	426	-106
Total Sediment P[2]	1033	886	-147

---

[1] Table 6

[2] Na_2CO_3 fusion

Table 36. Relative changes in total phosphorus and in inorganic phosphorus fractions of Buck Island sediments on long-term incubation in the dialysis system.

Chemical treatment[1]	Sediment inorganic P		
	Before incubation	After 90 day incubation	Alteration
	µg/g		
1 NH_4Cl	1	0	-1
2 NH_4F	71	53	-18
3 NaOH (0.1M)	86	70	-16
4 $Na_2S_2O_4$-$Na_3C_6H_5O_2$	34	32	-2
5 NaOH (1.0M)	78	83	+5
6 HCl	24	22	-2
7 Ignition	0	0	0
8 Fusion	47	32	-15
Total Treatments 1-8	341	293	-48
Total Sediment P[2]	606	553	-53

---

[1] Table 6

[2] Na_2CO_3 fusion

Table 37. Relative changes in total phosphorus and in inorganic phosphorus fractions of Pelican Marina sediments on long-term incubation in the dialysis system.

Chemical treatment[1]	Sediment inorganic P		
	Before incubation	After 90 day incubation	Alteration
	μg/g		
1 NH_4Cl	1	0	-1
2 NH_4F	35	85	+50
3 NaOH (0.1M)	101	69	-32
4 $Na_2S_2O_4$-$Na_3C_6H_5O_2$	30	46	+16
5 NaOH (1.0M)	52	88	+36
6 HCl	46	52	+6
7 Ignition	0	0	0
8 Fusion	61	52	-9
Total Treatments 1-8	326	392	+66
Total Sediment P[2]	693	614	-79

---

[1] Table 6

[2] Na_2CO_3 fusion

effects after 90 days incubation the NH_4F (Al-P) and NaOH (0.1 M) (non-occluded Fe-P) fractions appeared to be responsible for most of the decreases in inorganic P observed in Howard Bay and Buck Island sediments. Pelican Marina sediments exhibited decreases in the NaOH (0.1 M) fraction as well but this decrease was more than compensated for by increases in the other fractions. It appeared that organic P (in this case taken as the difference between total P and P in fractions 1-8) was mineralized in both Howard Bay and Pelican Marina sediments. In the case of Howard Bay sediments, a portion of this P was released, whereas in the Pelican Marina sediments the P was stabilized in mineral forms. Most of the reductions in Buck Island sediments was due to reductions in mineral P.

Comparing the results of these analyses with changes observed in samples taken from the field (Section IV, B), it is noteworthy that in both cases the P in the NH_4F, NaOH (0.1 M) and $Na_2S_2O_4$-$Na_3C_6H_5O_2$ extracts representing forms of Al-P and Fe-P (Treatments 2, 3 and 4; Table 6) appeared to account for most of the variation in inorganic P. Reductions in NaOH (0.1 M) extractable P, representing non-occluded Fe-P forms, were most consistently responsible for decreases in sediment inorganic P. Increases in inorganic P when observed were generally associated with increases in the NH_4F extract representing non-occluded Al-forms.

The extent of resorption of P during dialysis may be estimated from ^{32}P equilibration studies. At the end of 30 days, resorption by sediments of ^{32}P spiked into the water half-cell ranged from 8.5 to 26.3% (Table 38). Treatments 4 and 8, replicates, were not comparable. Experiments have shown (Section V, A) that the rate of P interchange between the cells is a function of diffusion rate which is reduced by the presence of the 0.45 μ filter. Both release and diffusion were restricted in Treatment 4 compared to Treatment 8 likely by a bubble of air adjacent to the filter. However, the data indicate that, as expected, P release was the dominant reaction in these systems.

The major quantity of P sorbed was associated with the NH_4Cl (readily exchangeable) and NH_4F (Al-P) fractions (Table 39). The ^{32}P not recovered may be present in part as organic forms. These experiments tend to substantiate results from both laboratory incubation and field studies which indicate that increases in inorganic P may be generally accounted for by increases in the NH_4F fraction.

Table 38. Equilibration of solution ^{32}P with lake sediments in the dialysis system.

Treatment number	Sediment sample[2] designation	Total P in solution Initial A	Total P in solution Final B	Total P in solution Released (A-B)	^{32}P in solution Initial C	^{32}P in solution Final D	^{32}P in solution Sorbed (C-D)	%
		---------µg---------			---------cpm(X107)---------			
4	H-13	458	1178	720	8.38	7.67	0.71	8.5
5	B-13	472	682	210	8.64	6.37	2.27	26.3
6	P-15	511	704	193	9.35	7.48	1.87	20.0
8	H-13	487	1899	1412	8.91	6.89	2.02	22.7

---

[1] Table 29

[2] Table 1

Table 39. Distribution of ^{32}P in sediment extracts after equilibration (30 days) with water containing ^{32}P in a dialysis system.

Chemical Treatment[1]	Dialysis Treatment[2]			
	4	5	6	8
	%[3]			
NH_4Cl (0.5$\underline{M}$)	10.2	1.4	1.0	9.6
NH_4F (0.5$\underline{M}$, pH 8.2)	58.2	65.5	67.9	37.7
NaOH (0.1$\underline{M}$)	0.0	0.0	0.0	0.0
$Na_2S_2O_4$ (0.1$\underline{M}$)	0.0	8.8	5.9	5.5
$Na_3C_6H_5O_2$ (0.3$\underline{M}$, pH 7.3)				
NaOH (1.0$\underline{M}$)	0.0	0.0	0.0	3.0
HCL (1.0$\underline{M}$)	8.8	5.9	17.0	1.2
TOTAL	77.2	81.7	91.8	57.0

---

[1] Table 6

[2] Table 29

[3] Percentage of total ^{32}P initially sorbed by sediment

Dialysates from Treatments 1, 2, 3 and 7 (Table 29) sampled after 41 days of incubation and containing 0.7 to 3.4 μg inorganic P/ml supported algal growth (Table 40). As a preliminary test, these solutions were assayed without additional essential nutrients. Nutrients available for growth therefore had to originate from the sediment. Growth in the dialysates was preceded by a longer lag phase than in the standard media likely reflecting a deficiency of nutrients other than P which was not limiting. It is noteworthy that considerable algal growth occurred on the unamended sediment dialysates substantiating the importance of sediments as sources of nutrients other than P. A distilled water blank containing only the algal inoculum (washed four times with distilled water) initially supported some algal growth indicating that small quantities of nutrients were retained on the cell surface.

The algal growth responses of dialysates (Table 41) calculated from the maximum cell concentration using the standard curve previously established (Figure 16) agreed reasonably well with determined inorganic P levels. The algal growth potential of P in the dialysates therefore appeared equivalent to orthophosphate-P. Growth in the dialysates was likely limited by the absence of nutrients present in the standard growth media.

The Presence of a Phosphorus Sink

To provide a sink for P released from sediments analogous to the effects of biological growth, the water half-cells in the dialysis units were amended with an anion exchange resin. The effect of the resin on the rate of P release was evaluated by monitoring both resin and solution P concentrations during incubation. These experiments were continued for 30 days and terminated. The sediments from control and resin-amended systems were fractionated into P mineral fractions after incubation to determine if incubation effected detectable changes in sediment P mineral status. Algal growth potentials of the solutions from the controls, not containing resin, were subsequently determined and the results compared with the resin systems.

Materials and Methods

Sediments taken in April, 1971, from Howard Bay, Buck Island, and Pelican Marina locations on Upper Klamath Lake were incubated in the dark at 25 C in a dialysis system containing distilled H_2O as previously described (Section V, A). The experimental design is outlined in Table 42. Periodically, the water cells

Table 40. Algal growth in sediment dialysates.

Treatment[1]	P Concentration[3]	Maximum specific growth rate[2]	Maximum cell concentration
	µg/ml	µ max	cells/ml
1	3.36	2.14	2.8×10^6
2	0.67	1.53	3.5×10^6
3	0.86	1.75	2.4×10^6
7	2.94	1.72	3.0×10^6
Standard Media	0.19	1.26	1.9×10^6
Blank	0.0	1.17	1.0×10^4

---

[1] Table 29

[2] $$\mu_{max} = \frac{\ln (x_2/x_1)}{t_2-t_1} \text{ days}^{-1}$$

where x_2 = biomass concentration at end of selected time interval

x_1 = biomass concentration at beginning of selected time interval

t_2-t_1 = elapsed time (days) between selected determinations of biomass.

[3] Sediment dialysates only; additional nutrients were not added

Table 41. Algal growth in standard media mended with sediment dialysates.

Treatment[1]	P Concentration in media	Maximum specific growth rate[2]	Maximum cell concentration
	μg/ml	μ max	cells/ml
1	0.07	1.37	1.2×10^6
2	0.05	1.48	7×10^5
3	0.03	1.74	9.5×10^5
7	0.06	1.43	9.7×10^5

---

[1] Table 29

[2] $$\mu_{max} = \frac{\ln(x_2/x_1)}{t_2 - t_1} \quad \text{days}^{-1}$$

where x_2 = biomass concentration at end of selected time interval

x_1 = biomass concentration at beginning of selected time interval

$t_2 - t_1$ = elapsed time (days) between selected determinations of biomass.

Table 42. Experimental design employed in investigations of sediment phosphorus released to solution containing anion exchange resin.

Treatment number	Sediment sample designation[1]	Sediment Composition				Water cell
		Wet weight	Total solids	Total P	Inorganic P	
		g	%	-------μg/g----------		
1	H-13	485	9.1	1033	574	Anion exchange resin
2	H-13	508	9.1	1033	574	
3	B-13	500	9.1	629	295	
4	P-15	461	10.4	662	348	
5	H-13	470	9.1	1033	574	Distilled H_2O only
6	H-13	455	9.1	1033	574	
7	B-13	477	9.1	629	295	
8	P-15	376	10.4	662	348	

[1] Table 1

were analyzed for P released from the sediment. The water half-cell containing the resin was evacuated using a vacuum siphon and the resin collected in a column over a screen (100 mesh). Total P in the solution was determined following $HClO_4$ digestion. The cell was refilled with fresh water and resin. The P on the resin removed from the cell was extracted (0.1 N HCl) and analyzed. Sediment P mineral fractionations and algal growth potential measurements were conducted as described in Sections IV, B and V, A, respectively.

Results and Discussion

The presence of the anion exchange resin in the water half-cell did not increase P release from Upper Klamath Lake sediments over a 30 day incubation period (Tables 43, 44, 45; Figure 25). In fact, after 30 days, total P in solution plus P on the resin was slightly less than total P released to solution in treatments containing water alone. Differences in solution pH likely resulting from sorption of the hydroxyl ion by the resin may have influenced the P release rate at the sediment-water interface. Higher water pH values, most closely approximating the theoretical pH for maximum solubility of Al and Fe phosphates (Lindsay and Moreno, 1960) occurred in the absence of the resins. However, sediment pH (Table 46) remained unchanged after incubation for 30 days.

It appears that the presence of the biota in the water cell would not result in additional sediment P release through uptake and retention of P from solution, however it is not possible to estimate the effect of different water pH values on P release in these systems.

It is noteworthy that the maximum rate of P release (Figure 25) occurred for Howard Bay sediment which contained relatively large quantities of P in the interstitial waters (Table 30). The rate was most rapid during the first 7 days of incubation. All interstitial water P was not released from Howard Bay sediments exposed to resin. However, P was released gradually to 20 days in Buck Island and Pelican Marina sediments amounting to many times the interstitial water P after 30 days.

The changes in the quantities of sediment total P and inorganic P in sediment P mineral fractions after incubation for 30 days in the presence and absence of an anion exchange resin are given in Tables 47-49. Resin and distilled water treatments were quite similar in total inorganic P as might be expected from the measurements of P released to solution. However,

Table 43. Total phosphorus and inorganic phosphorus (cumulative) released to solution during incubation of replicate Howard Bay sediments in the presence (Treatment 1,2) and absence (Treatment 5,6) of an anion exchange resin.[1]

Incubation time	Solution pH Treatments				Total P in solution Treatments				P on resin Treatments		Inorganic P in solution Treatments	
	1	2	5	6	1	2	5	6	1	2	5	6
days	---------units----------				---------------------------µg P/g sediment----------------							
2	5.9	4.4	6.2	6.2	0.0	0.0	1.1	0.5	3.2	1.6	0.9	0.4
5	5.6	5.6	6.4	6.5	0.5	0.3	15.8	17.6	9.9	9.1	15.5	17.3
8	5.8	5.6	6.4	6.4	0.7	0.5	31.5	29.1	15.1	14.4	29.1	27.0
12	5.7	5.4	6.1	6.2	1.6	1.7	38.7	37.5	22.8	23.1	36.7	34.9
15	4.8	5.6	6.4	6.4	2.5	2.4	45.3	42.7	27.1	27.4	42.9	40.0
19	5.6	4.5	6.2	6.3	3.9	3.7	52.5	49.8	34.2	33.3	49.8	46.6
22	5.1	4.2	6.2	6.3	4.8	4.4	57.6	55.0	36.8	37.4	55.0	51.8
26	5.3	4.2	6.2	6.3	5.6	5.4	63.9	61.0	42.1	43.1	61.1	57.6
30	5.2	4.2	6.1	6.2	6.2	6.1	69.6	67.4	48.3	49.4	66.5	63.6

---

[1] Table 42

Table 44. Total phosphorus and inorganic phosphorus (cumulative) released to solution during incubation of Buck Island sediments in the presence (Treatment 3) and absence (Treatment 7) of an anion exchange resin.[1]

Incubation time	Solution pH Treatments		Total P in solution Treatment		P on resin Treatment	Inorganic P in solution Treatment
	3	7	3	7	3	7
days	---units-----		---------------µg/g sediment---------------			
2	4.4	6.1	0.0	0.0	0.3	0.0
5	5.8	6.5	0.0	1.6	1.1	1.5
8	4.5	6.5	0.2	3.5	1.5	3.1
12	4.2	6.2	0.5	5.0	2.7	4.5
15	4.5	6.4	1.0	6.8	3.7	6.1
19	4.1	6.2	1.7	9.8	5.2	8.6
22	4.1	3.6	2.0	12.7	6.1	11.3
26	4.0	6.0	2.2	15.6	7.5	14.1
30	4.1	6.4	2.4	18.1	9.0	16.1

---

[1] Table 42

Table 45. Total phosphorus and inorganic phosphorus (cumulative) released to solution during incubation of Pelican Marina sediments in the presence (Treatment 4) and absence (Treatment 8) of an anion exchange resin.[1]

Incubation time	Solution pH Treatment		Total P in solution Treatment		P on resin Treatment	Inorganic P in solution Treatment
	4	8	4	8	4	8
days	----units---		--------------	µg/g sediment	-------------	
2	4.1	6.0	0.0	0.0	0.1	0.0
5	5.4	6.5	0.0	0.6	0.4	0.4
8	4.3	6.4	0.2	0.8	0.8	0.5
12	4.2	6.2	0.5	2.4	2.5	1.9
15	4.4	6.5	0.8	4.2	3.4	3.6
19	4.2	6.3	1.3	6.7	4.9	5.7
22	4.1	6.2	1.4	8.3	5.8	7.3
26	4.2	6.2	1.8	10.1	7.3	8.8
30	4.0	6.1	2.1	13.4	9.4	11.1

---

[1] Table 42

Table 46. Sediment pH after equilibration (30 days) in dialysis systems.

Treatment[1]	Sediment pH
1	6.6
2	6.6
3	6.5
4	6.4
5	6.5
6	6.8
7	6.5
8	6.6

[1] Table 1

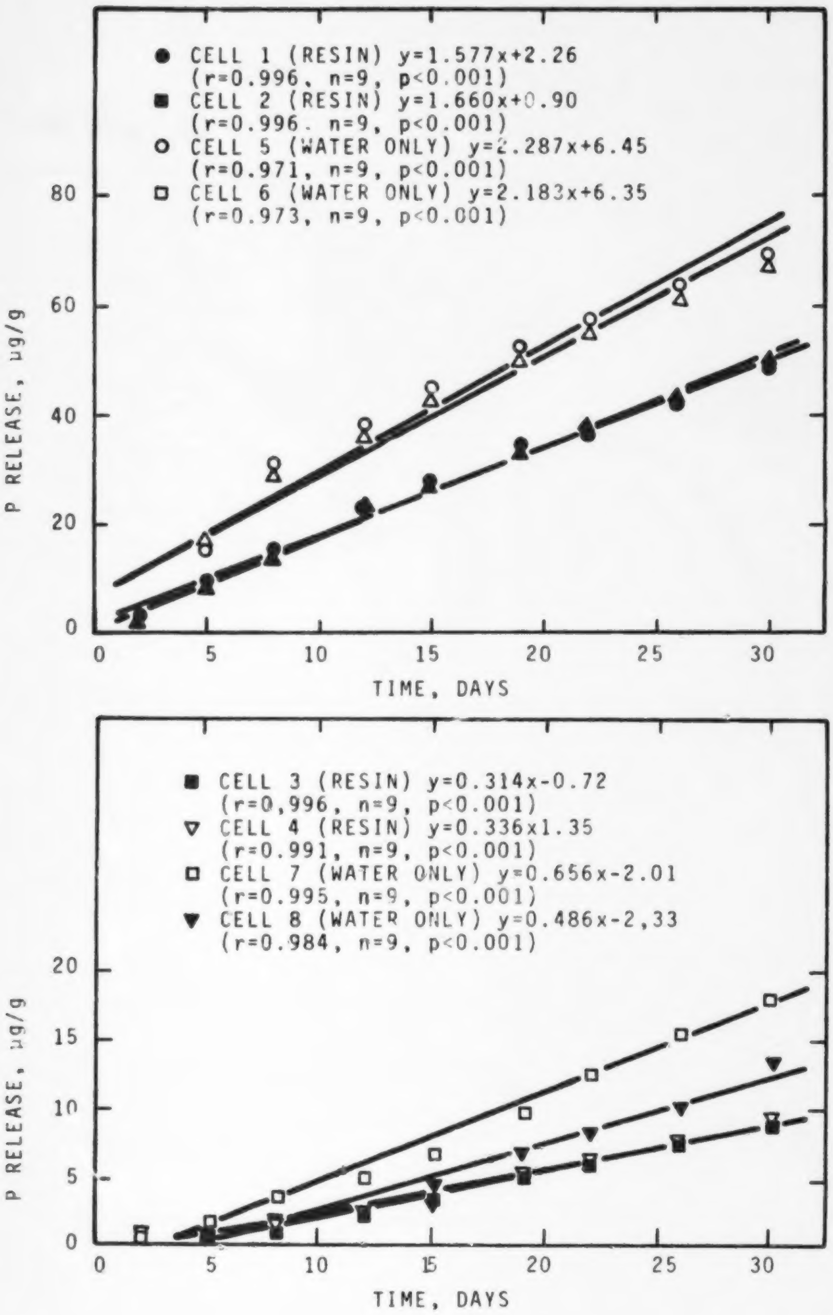

FIGURE 25. REGRESSIONS OF SEDIMENT PHOSPHORUS RELEASE IN DIALYSIS SYSTEMS WITH AND WITHOUT RESIN IN THE WATER HALF-CELL (TABLE 42).

Table 47. Comparison of the distribution of phosphorus in Howard Bay sediment inorganic phosphorus fractions after incubation (30 days) in dialysis system in the presence and absence of an anion exchange resin.

Chemical[1] Treatment	Sediment Inorganic P Initial	With Resin	Without Resin
	-------μg/g	-------------	
NH_4Cl	6	4	0
NH_4F	213	152	156
NaOH (0.1M)	142	56	68
$Na_2S_2O_4$- $Na_3C_6H_5O_2$	62	85	74
NaOH (1.0M)	29	59	85
HCl	24	22	24
Ignition	0	0	0
Fusion	56	40	37
Treatment 1-8	532	418	443
Total Sediment P[2]	1033	913	885

---

[1] Table 6

[2] Na_2CO_3 fusion

Table 48. Comparison of the distribution of phosphorus in Buck Island sediment inorganic phosphorus fraction after incubation (30 days) in dialysis systems in the presence and absence of an anion exchange resin.

Chemical[2] Treatment	Initial	With Resin	Without Resin
	----------μg/g-----------		
NH_4Cl	1	1	0
NH_4F	71	42	42
NaOH (0.1M)	86	42	52
$Na_2S_2O_4$-$Na_3C_6H_5O_2$	34	52	40
NaOH (1.0M)	78	42	66
HCl	24	21	8
Ignition	0	0	0
Fusion	47	28	29
Treatment 1-8	341	228	247
Total Sediment P[2]	606	564	567

---

[1] Table 6

[2] Na_2CO_3 fusion

Table 49. Comparison of the distribution of phosphorus in Pelican Marina sediment inorganic phosphorus fractions after incubation (30 days) in dialysis systems in the presence and absence of an anion exchange resin.

Chemical[1] Treatment	Initial	With Resin	Without Resin
	--------------	µg/g	---------
NH_4Cl	1	1	0
NH_4F	35	40	44
NaOH (0.1M)	101	46	61
$Na_2S_2O_4$- $Na_3C_6H_5O_2$	30	48	38
NaOH (1.0M)	52	54	65
HCl	46	44	45
Ignition	0	0	0
Fusion	61	48	45
Total	326	281	298
Total Sediment P[2]	693	632	636

---

[1] Table 6

[2] Na_2CO_3 fusion

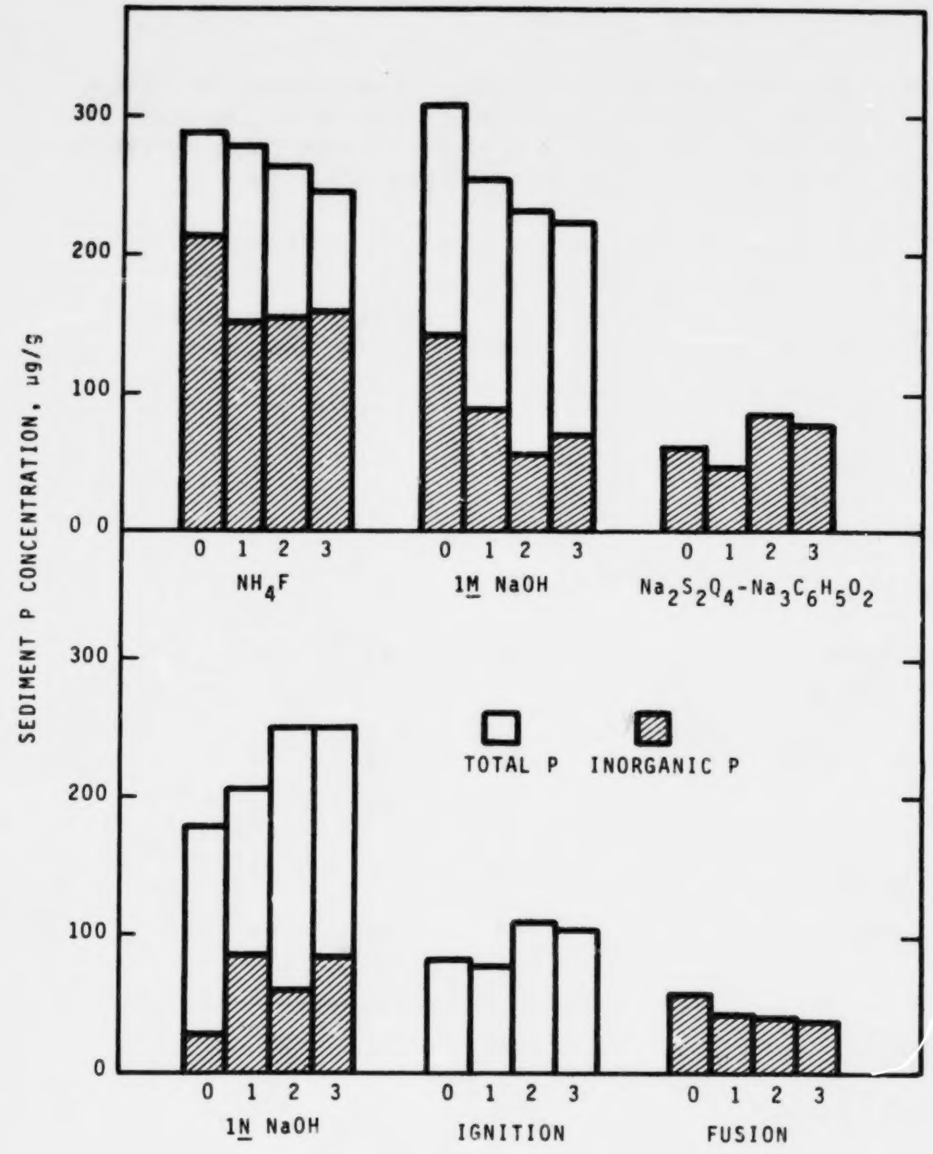

FIGURE 26. COMPARISON OF PHOSPHORUS CONTENTS IN INORGANIC PHOSPHORUS FRACTIONS OF HOWARD BAY SEDIMENTS AFTER INCUBATION IN THE DIALYSIS SYSTEM IN THE PRESENCE AND ABSENCE OF AN ANION EXCHANGE RESIN (COLUMNS 1, 2, AND 3 DESIGNATE VALUES OBTAINED AFTER INCUBATION, RESPECTIVELY, FOR 90 DAYS - DISTILLED WATER ONLY, 30 DAYS - RESIN, 30 DAYS - DISTILLED WATER ONLY).

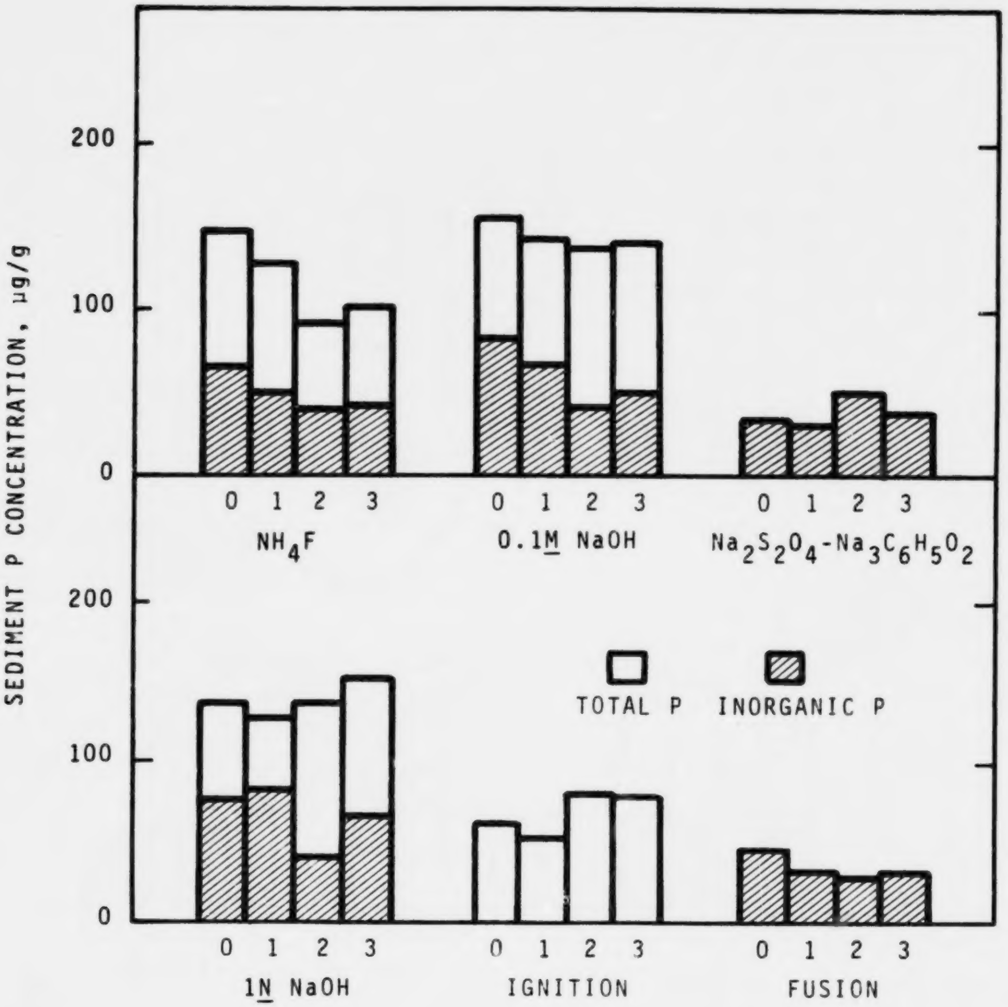

FIGURE 27. COMPARISON OF PHOSPHORUS CONTENTS IN INORGANIC PHOSPHORUS FRACTIONS OF BUCK ISLAND SEDIMENTS AFTER INCUBATION IN THE DIALYSIS SYSTEM IN THE PRESENCE AND ABSENCE OF AN ANION EXCHANGE RESIN (COLUMNS 1, 2, AND 3 DESIGNATE VALUES OBTAINED AFTER INCUBATION, RESPECTIVELY, FOR 90 DAYS - DISTILLED WATER ONLY, 30 DAYS - RESIN, 30 DAYS - DISTILLED WATER ONLY).

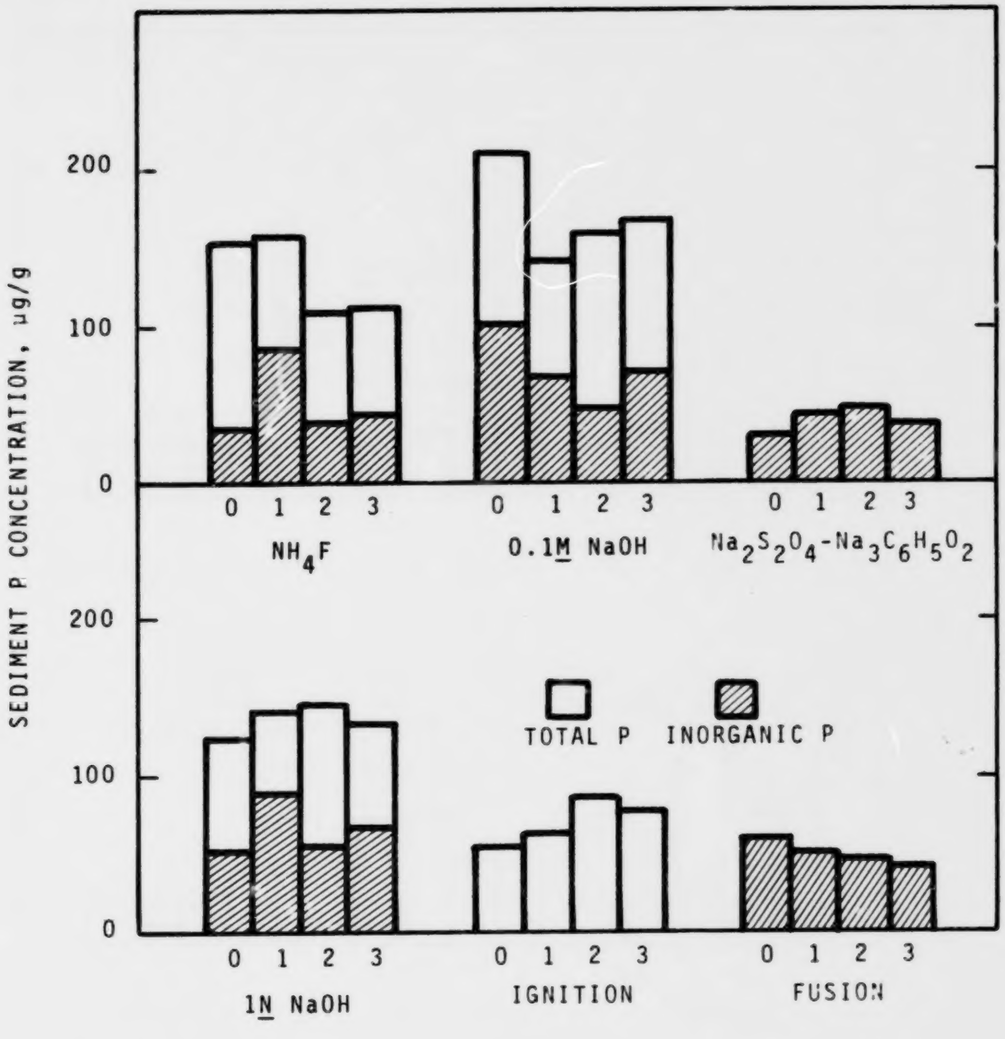

FIGURE 28. COMPARISON OF PHOSPHORUS CONTENTS IN INORGANIC PHOSPHORUS FRACTIONS OF PELICAN MARINA SEDIMENTS AFTER INCUBATION IN THE DIALYSIS SYSTEM IN THE PRESENCE AND ABSENCE OF AN ANION EXCHANGE RESIN (COLUMNS 1, 2, AND 3 DESIGNATE VALUES OBTAINED AFTER INCUBATION, RESPECTIVELY, FOR 90 DAYS - DISTILLED WATER ONLY, 30 DAYS - RESIN, 30 DAYS - DISTILLED WATER ONLY).

regardless of treatment, incubation effected changes in P mineral distribution. The inorganic P extractable by NH_4F was markedly reduced in the cases of Howard Bay and Buck Island and P in the NaOH (0.1 M) fractions was reduced in all sediments. In contrast, P extractable by $Na_2S_2O_4$-$Na_3C_6H_5O_2$ increased on incubation for all sediments. Evidently, Al and ferric Fe were in part released and in part converted to more reduced forms of Fe on incubation under anaerobic conditions. These results are illustrated in Figure 26, 27 and 28. For comparative purposes, values obtained after incubation of the sediments for 90 days with distilled water (Tables 31-33) are also illustrated. It is apparent that in the case of these fractions, incubation at 30 days in the dialysis system was sufficient to reduce sediment P to near minimum levels and further incubation to 90 days did not result in additional release of P.

The algal growth potential of sediment dialysates spiked into standard media are given in Table 50. As in previous measurements the μ_{max} of dialysates was not proportional to P concentration. Solution P concentrations between 0.08 and 0.11 μg/ml (Treatments 5, 6 and 7) supported approximately equivalent maximum growth whereas significantly less growth was measured in the dialysate containing 0.04 μg/ml (Treatment 8).

Direct Equilibration With an Anion Exchange Resin

The development of a method for the assay of the potential for P release from sediments using direct sediment equilibration with an anion exchange resin was described in Section V, A. The application of this method to the sediments of Upper Klamath Lake is described in this section. The results are related to release in the dialysis system.

Materials and Methods

Using the system described in Section V, A, sediments from Howard Bay, Buck Island and Pelican Marina (2.5 g dry weight) taken in April, 1971, were incubated in the dark at 25 C with 1.25 g resin. The results for 30 days of incubation are summarized.

Results and Discussion

In contrast to dialysis systems (Tables 43-45) sediments incubated with resin in the direct equilibration systems exhibited considerably more release than sediments not receiving resin (Table 51). In fact, Howard Bay sediments released approximately

Table 50. Algal growth in standard media amended with sediment dialysates.

Treatment[1]	P concentration in media	Maximum specific growth rate[2]	Maximum cell concentration
	µg/ml	μ_{max}	cells/ml
5	0.10	1.46	1.3×10^6
6	0.11	1.35	1.2×10^6
7	0.08	1.56	1.5×10^6
8	0.04	1.60	5.3×10^5

---

[1] Table 42

[2] $$\mu_{max} = \frac{\ln(x_2/x_1)}{t_2 - t_1} \text{ days}^{-1}$$

where x_2 = cell concentration at end of selected time interval

x_1 = cell concentration at beginning of selected time interval

$t_2 - t_1$ = elapsed time (days) between selected determinations of biomass

33% of the total sediment P during a 30 day incubation with the resin (Figure 29). The release of P from Buck Island and Pelican Marina sediments, over a 35-day incubation period amounted, respectively, to 84 and 50 μg/g of sediment in the presence of the anion exchange resin (Figure 30). In systems which did not contain resin, release of total P amounted to less than 15% of the P contained on the resin. Thus, in contrast to dialysis systems, the presence of a P sink has a substantial influence on the quantity of P released to solution indicating that a biological sink in surface waters may have similar effects. The influence would likely be considerably less pronounced due to a lack of direct contact with sediment interstitial waters.

The presence of an anion exchange resin tended to buffer the sediments at a relatively constant pH, whereas the pH of Buck Island and Pelican Marina sediments was considerably lower in the absence of resin after approximately 7 days of incubation. The lowering of pH would likely tend to increase P release and therefore minimize release differences between treatments.

Howard Bay sediments released 4-6 times as much P to the resin as the other sediments. Thus, both dialysis and direct equilibration systems substantiate field observations of the labile nature of P in Howard Bay sediments relative to sediments from other locations. The data indicate that the lack of resin effect in the dialysis systems resulted from a limitation on water interchange and P diffusion through the 0.45 μ filter or reduced uptake rate resulting from lower P concentrations in solution.

Algal Growth in the Dialysis Cell

It has been previously shown that direct incubation of sediments with a P sink in the form of an anion exchange resin increases the rate and extent of sediment P release (Table 51). Furthermore, dialysates from the sediment-distilled water dialysis systems will support algal growth at rates comparable to those in standard media (Table 40, 41). This experiment was designed as a preliminary test to determine (*i*) if algae could be cultured directly in the dialysis system, (*ii*) specific growth rates of algae under these conditions and (*iii*) the effect on P release of a P sink in the form of actively reproducing algal cells.

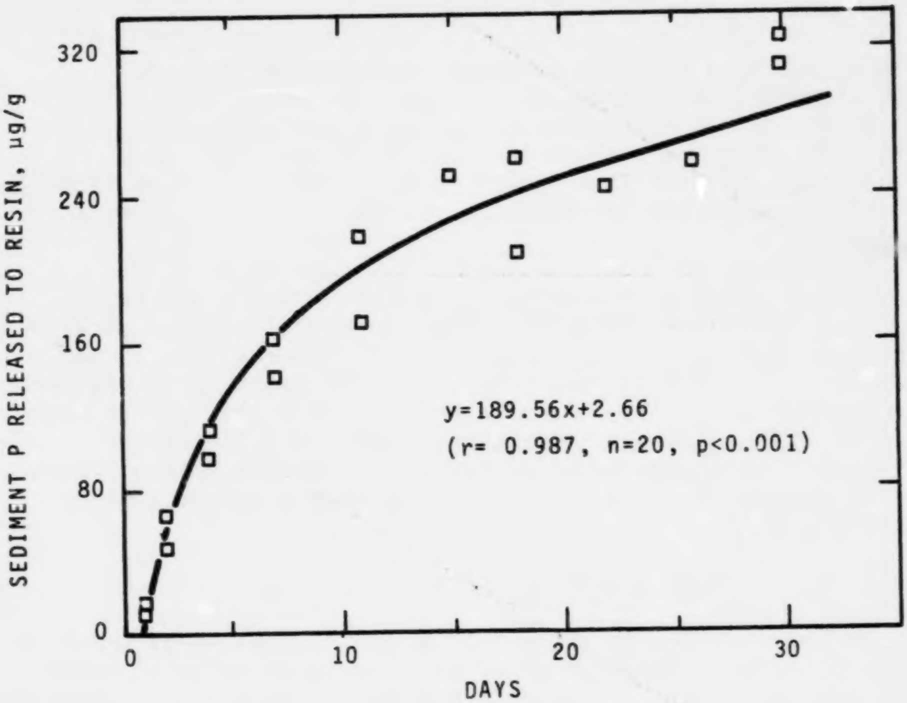

FIGURE 29. RELEASE OF PHOSPHORUS FROM HOWARD BAY SEDIMENTS TO AN ANION EXCHANGE RESIN IN THE DIRECT EQUILIBRATION SYSTEM (TABLE 51).

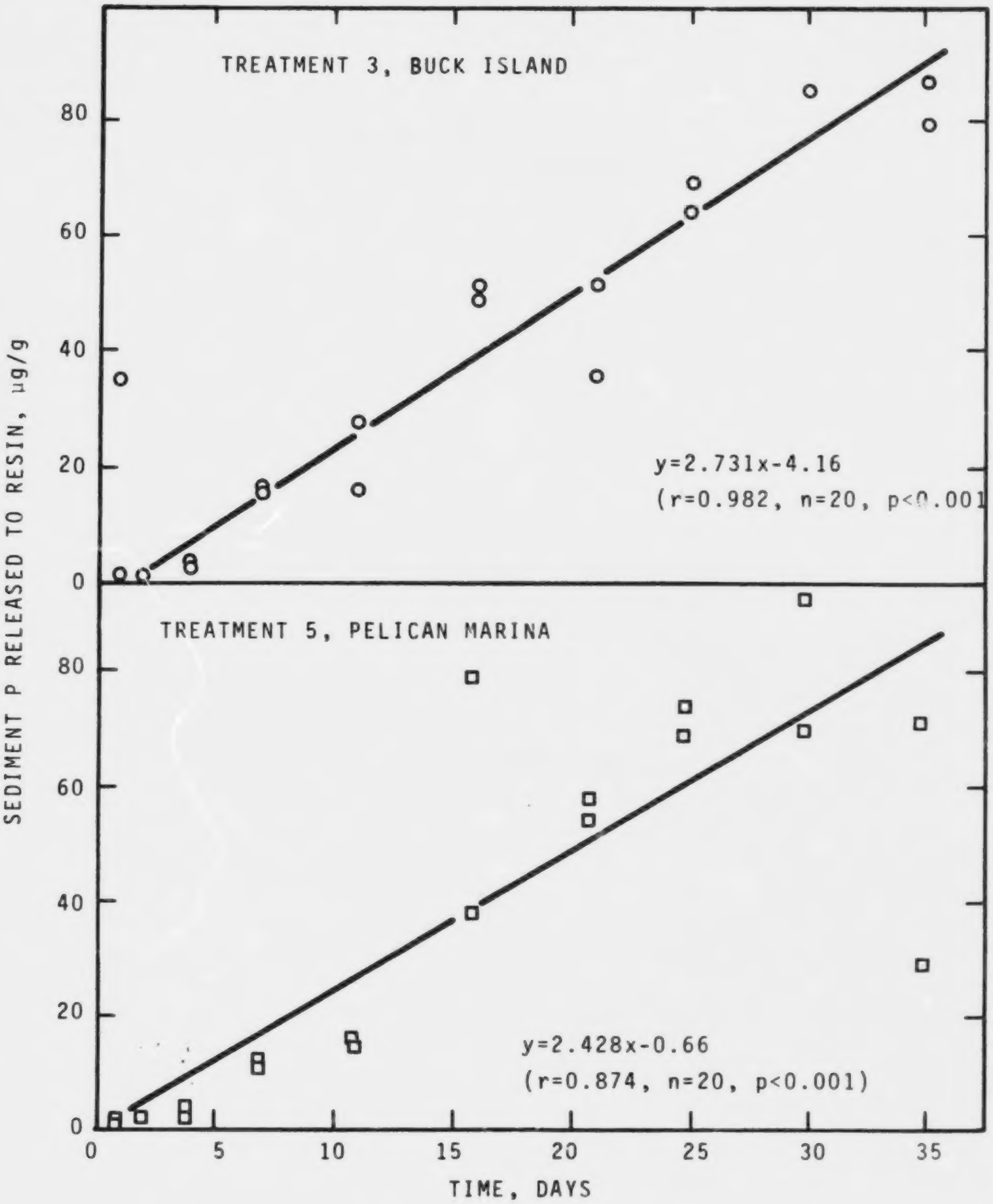

FIGURE 30. RELEASE OF PHOSPHORUS FROM BUCK ISLAND AND PELICAN MARINA SEDIMENTS TO AN ANION EXCHANGE RESIN IN THE DIRECT EQUILIBRATION SYSTEM (TABLE 51).

Table 51. Release of phosphorus from moist Howard Bay (Treatments 1 and 2), Buck Island (Treatments 3 and 4 and Pelican Marina (Treatments 5 and 6) sediments in the presence (Treatments 1, 3 and 5) and absence (Treatments 2, 4 and 6) of anion exchange resin (direct equilibration system).

Incubation time	P in solution		Total P on resin	pH
	Total P	Inorganic P		
days	µg/g sediment			
		Treatment 1		
1	18	10	15	6.4
2	16	0	57	6.4
4	18	2	115	6.4
7	26	8	152	6.4
11	35	13	194	6.4
15	36	14	252	6.6
18	33	12	234	6.4
22	32	8	245	6.6
26	36	10	256	6.8
30	34	10	308	6.8
		Treatment 2		
1	23	12		7.0
2	26	4		6.9
4	34	10		6.9
7	36	8		6.8
11	33	27		6.8
15	28	7		6.8
18	40	21		6.8
22	40	20		6.8
26	42	21		7.0
30	44	11		7.0

Table 51 (Continued).

Incubation time	P in solution Total P	P in solution Inorganic P	Total P on resin	pH
days	---------------µg/g sediment----------			
		Treatment 3		
1	6	-	1	6.4
2	12	-	1	5.8
4	12	-	2	6.1
7	14	1	16	5.7
11	17	1	22	5.6
16	14	4	50	6.2
21	14	2	44	6.0
25	16	2	68	6.2
30	15	4	86	6.3
35	20	2	84	6.3
		Treatment 4		
0	8	5		7.2
1	8	-		6.8
2	11	-		6.3
4	10	-		6.3
7	7	-		5.6
11	16	1		5.6
16	12	4		5.7
21	6	1		5.0
25	9	2		4.8
30	4	2		4.3
35	6	3		4.3

Table 51 (Continued).

Incubation time	P in solution		Total P on resin	pH
	Total P	Inorganic P		
days	----------------μg/g sediment---------			
	Treatment 5			
1	4	-	2	6.2
2	8	1	1	5.7
4	7	1	3	6.2
7	10	2	12	5.5
11	9	1	15	6.0
16	14	8	58	6.2
21	12	2	56	6.0
25	14	5	72	6.2
30	15	4	94	6.3
35	18	5	50	6.3
	Treatment 6			
0	9	4		7.4
1	6	-		6.6
2	6	1		6.1
4	15	1		6.4
7	12	1		5.6
11	8	1		5.8
16	7	4		6.1
21	9	2		5.6
25	5	2		5.2
30	4	1		5.0
35	6	2		4.8

Materials and Methods

Dialysis cells were prepared in the manner described previously (Section V, A) using sediments from Howard Bay, Buck Island and Pelican Marina. However the membrane filter between the half-cells was omitted since previous work had shown that the 0.45 μ membrane filter had a restrictive effect on P diffusion between cells. Standard media less P (300 mls) was added to the water half-cells and inoculated with Selenastrum capricornutum (10^3 cells/ml). Uninoculated dialysis cells were also prepared. The experimental design is outlined in Table 52. No effort was made to maintain asepsis as the omission of the membrane filter allowed the passage of microorganisms between the cells.

The cells were incubated in a vertical position under light at 25 C with gentle gyration (120 rpm). During the first week, aliquots (30 ml) were removed daily for P determination and algal cell count. Sufficient media was added to the upper cell to maintain constant volume. On the seventh day, the upper cell was drained and fresh media added. The dialysis cells which had been originally inoculated were then reinoculated using the drained media (5 ml).

Total P and inorganic P were determined as previously described (Section IV, A). Algal growth was measured by the direct cell count technique.

Results and Discussion

The dialysis cells developed a visible algal growth after 4 days of incubation with or without previous inoculation with Selenastrum. Subsequent microscopic examination of the media revealed no growth of Selenastrum occurred but rather another species of algae, tentatively identified as Chloroella sp., was present. The omission of the 0.45 μ membrane filter may have allowed the passage of Chlorella autospores from the sediment into the media and the subsequent growth of the algae as P was released.

The algal growth parameters of the Chlorella sp. are given in Table 53. The maximum specific growth rates, μ_{max}, and total cell counts at 7 days for Howard Bay sediment are higher than the parameters in previous experiments in which Selenastrum was cultured in the absence of sediments. However Selenastrum was cultured in media dilutions of aliquots from the dialysis systems with inorganic P concentrations of 0.06 to 0.11 μg/ml

Table 52. Experimental design employed in investigations of sediment phosphorus release to inoculated algae growth media.

Treatment number	Sediment sample designation[1]	Sediment Composition				Water Cell
		Wet weight	Total solids	Total P	Inorganic P	
		g	%	-----μg/g-----------		
1	H-13	485	9.1	1033	574	Media and Inoculum
2	H-13	508	9.1	1033	574	
3	B-13	500	9.1	629	295	
4	P-15	461	10.4	662	348	
5	H-13	470	9.1	1033	574	Media only
6	H-13	455	9.1	1033	574	
7	B-13	477	9.1	629	295	
8	P-15	376	10.4	662	348	

Table 53. Growth of *Chlorella* sp. cultured in the dialysis system utilizing sediments as a source of phosphorus.

Sediment sample designation	Treatment[1] number	Specific growth[2] rate	Cell counts, 7 days
		μ_{max}	cells/ml
Howard Bay	1	3.045	6.5×10^6
	2	2.303	9.2×10^6
	5	2.862	9.4×10^6
	6	2.731	8.1×10^6
Buck Island	3	1.712	3.6×10^5
Pelican Marina	4	2.429	7.5×10^5
	8	1.992	1.1×10^5

[1] Table 52

[2] Calculated as previously described (table 40)

for Howard Bay sediment and 0.03 to 0.08 μg/ml for Buck Island and Pelican Marina sediments. The total P concentrations for this experiment ranged from 1 to 2.5 μg/ml during the period of maximum growth for Howard Bay sediment and from 0.08 to 0.24 for Buck Island and Pelican Marina sediments. The 16-20 fold increase in P concentration for the Howard Bay sediment dialysates and the use of a native organism likely account for the increase in growth parameters shown in this experiment.

After 7 days, total P released from the sediments to the water half-cell, determined by including digested algal tissue, amounted to 17.5, 0.7 and 0.7 μg/g of Howard Bay, Buck Island and Pelican Marina sediments, respectively. Reinoculation at 7 days followed by another 7 day incubation period resulted in release of an additional 4 μg P/g of Howard Bay sediments after a total of 12 days. However no additional P was lost after 12 days incubation, and no further P release occurred with the Buck Island and Pelican Marina sediments during the second 7 day incubation period.

The P release rate in the vertical dialysis systems without the 0.45 μ filter and containing the algal culture was quite similar to release in horizontal systems containing the filter and anion exchange resin (Figure 25). It appears that when the dialysis cells are in the vertical positions, diffusion of P through the membrane is not a limiting factor as suggested by earlier experiments with water in each half-cell. An experiment similar to that described in this section but incorporating a 0.45 μ filter partition between sediments and water to reduce the possibility of sediment biological contamination of the water half-cell would therefore be in order.

It is evident that in these systems, sediments supply ample P for biological growth. This method with suitable modifications may serve in routine assessments of the potential for P release from sediments and subsequent availability of released P to algae.

SECTION VI

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SECTION VII

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SECTION VIII

APPENDIX

CHEMICAL CHARACTERISTICS OF SEDIMENTS FROM SEVERAL LAKE SYSTEMS

A. SHAGAWA LAKE, MINNESOTA

This section describes the results of efforts to compile and statistically analyze, through correlation and mathematical modeling, data obtained on the C, N and P contents of sediments taken in September, 1970 from Shagawa Lake, Minnesota. The primary goals of these studies were to (*i*) characterize the sediments as to mineralogical composition, (*ii*) establish mean variation in total lake sediment C, N and P contents and (*iii*) determine if mathematical relationships between the elements existed which would provide insight into their distribution, deposition, or transformations in the lake system. Inherent in these investigations was the development of background information to assist in selection of lake sediment sample sites for future investigations of P release. Sample sites on Shagawa Lake are identified by location on a lake grid system (Figure 31).

Materials and Methods

Analyses of the mineral composition of the intact sediments were conducted using X-ray diffraction techniques. Following a series of ion saturation and heat treatments (Whitlig, 1965), sediment samples were oriented on glass slides, glycerated and analyzed in a Norelco X-ray diffractometer using Cu-K shell α radiation and a Ni filter (Kittrick and Hope, 1963).

The methods of analyses for sediment P concentrations have been previously described (Section IV). The concentrations of total C and N in the sediments were provided by EPA personnel at the Pacific Northwest Laboratory, Corvallis.

Total S was determined by Na_2CO_3 fusion techniques essentially as recommended by the Association of Official Agricultural Chemists (1955).

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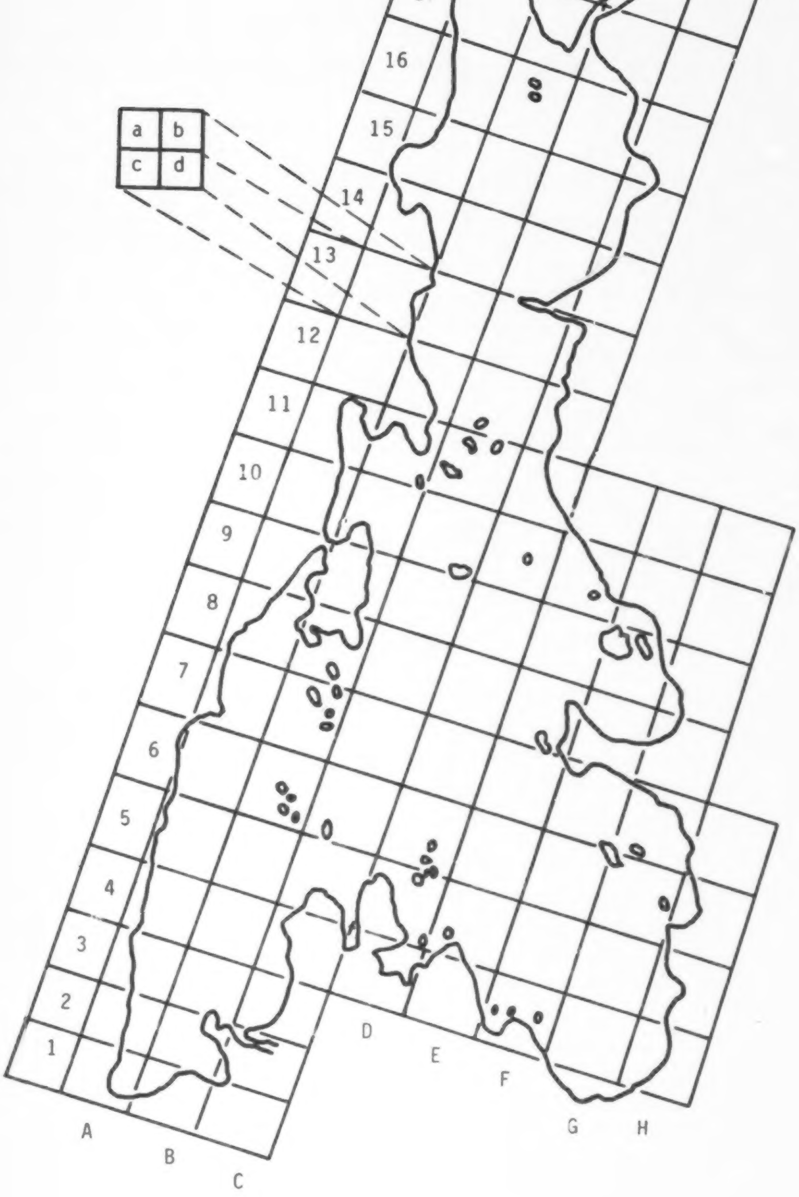
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FIGURE 31. GRID SYSTEM - SHAGAWA LAKE, MINNESOTA.

Results and Discussion

The mineralogical compositions of Shagawa Lake sediments, as determined by X-ray diffraction techniques, are given in Table 54. Sediment samples from 6 locations throughout the lake were similar in mineral composition, and no significant mineralogical differences were observed between samples. Kaolinite may have been present, but only in trace quantities. The diffractograms (Figure 32) indicate the presence of expanding lattice materials, however the apparent tendency to collapse under K saturation suggests the presence instead of weathered mica (beidellite-like material). The samples were not separated according to particle size and therefore it was not possible to determine definitively if montmorillonite, a clay-sized (<2 micron) mineral, was present. In general, the sediments appear to consist primarily of finely-divided granitic materials derived from glacial deposited parent materials.

Total S in Shagawa Lake sediments (Table 55) ranged from 0.28% (C11d) to 0.95% (B15d). The concentration of S was generally related to X-ray diffraction response at the diffraction angle attributed to gypsum, however due to differences in crystalinity, response and amorphous background these comparisons cannot be considered quantitative.

Highest S concentrations were in sediments taken from deeper locations, i.e. A6d, B15d and D8c. It might be expected, however that S at these lower depths would be present primarily in reduced forms rather than as gypsum.

Mean C, N and P contents for Shagawa sediments sampled at 31 locations on Shagawa Lake are given in Tables 56, 57. Due to the magnitude of the differences in total C and N and P, C and N contents are expressed as percentages whereas P contents are expressed on a μg/g basis. Considering the wide range in sample site locations within the lake, elemental composition of the sediments did not deviate widely from the mean. In terms of the total concentration, maximum variation occurred in the case of N ($\overline{x}$, 1.20; Sd, 0.3).

The sewage effluent (grid location E10, Figure 31) from the town of Ely, Minnesota is likely the principal source of the excessive quantities of nutrients entering Shagawa Lake. However, little is known of the distribution or fate of these materials upon entrance into the lake system. To provide insight into the location of the effluent in the lake, data on elemental distribution in sediments was statistically

Table 54. Mineralogical composition of the sediments of Shagawa Lake.

Mineral type, relative concentration[1] and diffraction angle[2]		
Abundant (>20%)	Present (10-20%)	Trace (5-10%)
quartz (27)	gypsum (21.0, 11.5)	amphibole (10.5)
	chlorite (25.5, 23.5, 12.5, 6.5)	
	feldspar (28.0, 22.5)	
	mica (27)	
	amorphous (background)	

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[1] Concentration defined approximately by comparison of relative height of diffraction maxima for minerals of known crystalinity and response.

[2] Diffraction angle (2θ) on K saturation, air dried.

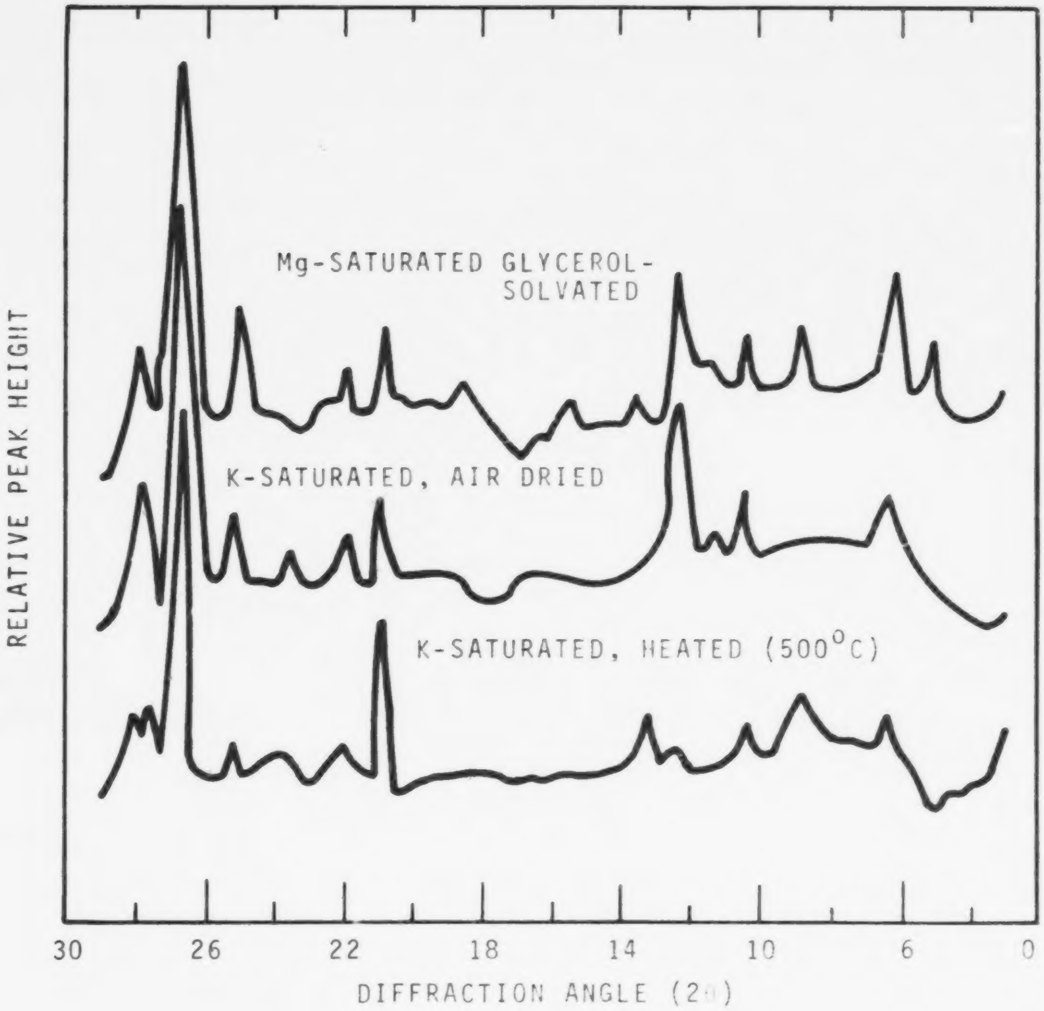

FIGURE 32. REPRESENTATIVE X-RAY DIFFRACTOGRAMS OF CHEMICALLY TREATED SEDIMENTS FROM SHAGAWA LAKE.

Table 55. Total sulfur concentration in sediments of Shagawa Lake, as related to relative gypsum concentration.

Sample designation	Sulfur content	Relative height height of X-ray diffraction maxima
	%	
A6d	0.77	+++
B13d	0.35	++
B15d	0.95	++
C11d	0.28	+
D8c	0.47	++
F5a	0.39	++

Table 56. Distribution of carbon and nitrogen in Shagawa Lake sediments.

Sample Site Grid Location	Water Depth	Content of C	Content of N	Sample Site Grid Location	Water Depth	Content of C	Content of N
	m	%	%		m	%	%
A5c	5	14.6	1.5	C8d	11	13.6	1.5
A6d	12	14.2	1.5	C11d	6	10.2	1.0
A10d	4.5	9.7	1.0	C12d	6	9.8	1.0
A17b	5	8.1	1.0	C13b	5.5	1.3	.2
B1b	4	13.6	1.3	C15b	10	11.2	1.4
B2c	4	2.6	.4	D8b	8	13.1	1.3
B3c	2	28.1	1.7	D8c	12	13.2	1.5
B5c	6	15.1	1.5	D11a	5.5	10.0	1.2
B10c	6	7.9	.9	E5b	6	16.0	1.6
B13b	5	10.6	1.3	E6c	6	14.1	1.5
B13d	5	9.7	1.0	E7c	6	13.0	1.5
B15a	6.5	10.7	1.1	E10b	6	11.8	1.1
B15b	12	10.9	1.3	F5a	6	13.4	1.3
C3a	3	17.4	1.5	F9a	5.5	9.6	.9
C8b	8	12.9	1.5	G4c	3	16.5	1.2
				G5a	6	15.0	1.5

Table 57. Summary of the concentrations of carbon, nitrogen and phosphorus in sediments of Shagawa Lake.

Variable[1]	Mean ($\bar{x}$)	Standard deviation ($\bar{S}d$)	95% confidence value (95% CV)
Total C(%)	12.20	4.6	1.70
Total N(%)	1.20	0.3	0.10
Total P(μg/g)	1231	238	88
Inorganic P			
absolute (μg/g)	691	160	59
fraction of total P(%)	56.8	10.9	3.9
Organic P			
absolute (μg/g)	541	169	61
fraction of total P(%)	43.2	10.9	3.9

analyzed on the basis of geographical location. In interpretations, particular emphasis was placed on the sediment distribution of elements in relation to the sewage outfall.

Although the direction and rate of intermediary current flows are unknown, the general direction of lake current is likely from west to east, i.e., from the mouth of the Burntside River at the west end of the lake to the outlet of the Shagawa River at the east end of the lake. Thus, it might be expected that the sewage effluent located on the south lake shore about midway on an east-west transect would accumulate in the sediments east of the outfall. Significant ($p < 0.01$) locational differences in the sediment concentration of C and N exist (Table 58). However, mean total C and N are approximately 50% higher in locations west or "upcurrent" from the sewage outfall. Total P was not significantly different between locations. Thus, assuming the C and N are not lost before deposition on the sediments, presumptive evidence suggests that the general depositional pattern of C and N originating from the sewage effluent, to the west, is perhaps reflecting current effects different from the expected. Furthermore, assuming that the sediment samples were representative, either P is not subject to similar mechanisms of transport and deposition or lake sediment (or water) transformations take place which tend to normalize the content of sediment P. A more detailed evaluation of total sediment P on the basis of lake location is presented in Table 59. Analyses of variance showed no significant locational effects. However, total P is highest in grid locations immediately north of the sewage outfall (grid locations A-E).

As in the case of sediment elemental distribution, the transformations of C, N and P in lake sediments are difficult to infer from direct analyses. However, some insight into gross changes, important to remedial measures, may be obtained. Linear intercorrelations of water depth, sediment total P, inorganic P, organic P and total C and N are given in Figure 33. Significant correlations existed between total P and inorganic P, independent measurements. As may be expected, organic P, taken as the difference between total and inorganic P, also correlated with total P. Significant correlations between organic P, total C and total N provide evidence that either the organic or total P measurement serves as a valid measure of P in organic combinations since a relatively constant ratio of these elements may be expected in biological tissue and in the sediment organic phase. It should be noted, however, that principal correlations are between C and N and correlation of P with these variables is comparatively low. In general,

Table 58. Distribution of total carbon, nitrogen and phosphorus in Shagawa Lake sampling locations west (grid sections 1-9) and east (grid sections 10-18) of the sewage outfall.[1]

	East location (A)			West location (B)			Location differences (A-B)		
Variable	Mean	Standard deviation	Number of values	Mean	Standard deviation	Number of values	Mean difference	Standard error of difference	T value
	%			%			%		
Total C	9.4	2.7	13	14.2	4.7	18	4.8	1.5	3.3[2]
Total N	1.0	0.3	13	1.4	0.3	18	0.4	0.1	3.1[2]
Total P	0.128	0.031	13	0.120	0.017	18	-0.009	0.009	1.0

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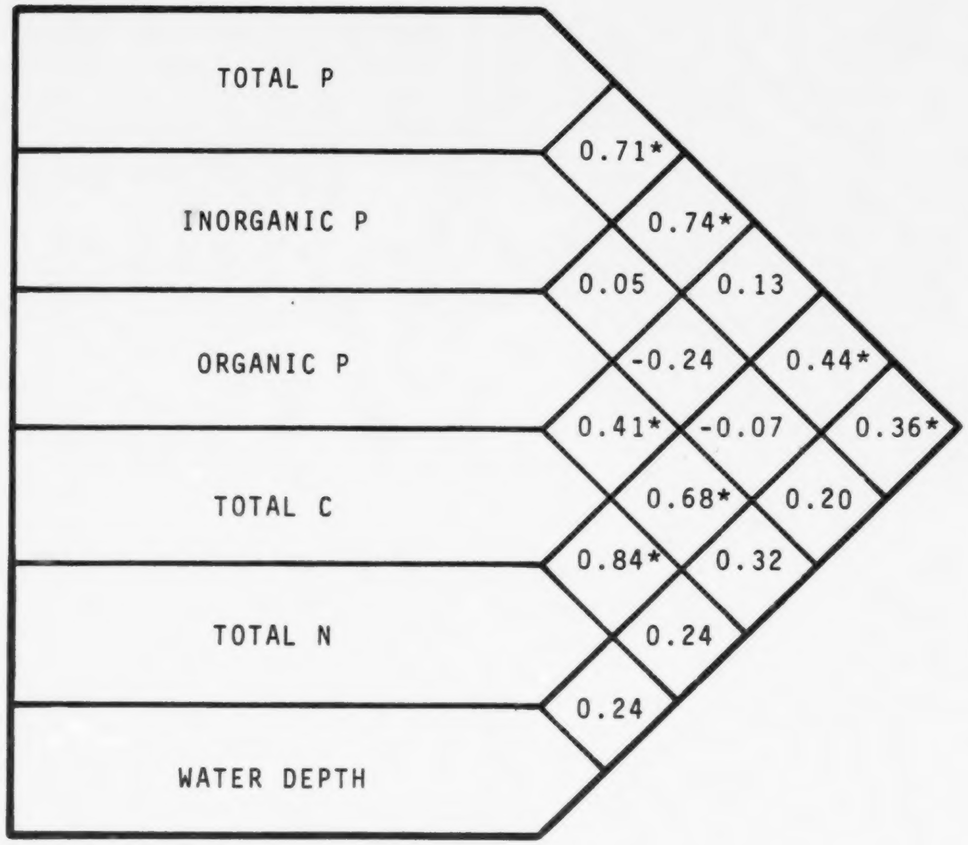
[1] Sewage effluent located at grid section E10 (Fig. 31).

[2] Significant at the 0.01 probability level.



	TOTAL P	INORGANIC P	ORGANIC P	TOTAL C	TOTAL N
INORGANIC P	0.71*				
ORGANIC P	0.74*	0.05			
TOTAL C	0.13	-0.24	0.41*		
TOTAL N	0.44*	-0.07	0.68*	0.84*	
WATER DEPTH	0.36*	0.20	0.32	0.24	0.24

FIGURE 33. CORRELATIONS OF WATER DEPTH, TOTAL, INORGANIC, AND ORGANIC PHOSPHORUS; TOTAL CARBON; AND TOTAL NITROGEN CONTENTS OF SEDIMENT SAMPLES FROM SHAGAWA LAKE. ASTERISK DESIGNATES $p < 0.05$.

Table 59. Geographical distribution of total phosphorus in sediments of Shagawa Lake.

Grid section[1,2]	Number of sample sites	Mean of total P	Standard deviation (Sd)
		------------------μg/g------------------	
North-south			
A	4	1240	100
B	9	1260	300
C	7	1260	300
D	3	1350	30
E	4	1180	200
F	2	1060	-
G	2	1070	-
East-west			
3	2	1130	-
5	5	1200	100
6	2	1150	-
8	4	1390	100
10	3	1020	200
11	2	1380	-
13	3	1220	600
15	3	1430	200

[1] Figure 31.

[2] Grid sections with a single value were excluded.

sediment P transformations which influence the concentration of one parameter may also be expected to have an influence on the correlated parameters.

A linear correlation between sediment total P and water depth indicates a significant relationship between these two variables. The correlation must be considered tenuous, due to the relatively small variation from the mean in sediment total P concentrations (Table 57). It would appear, however, that water depth must be considered in sampling programs designed to determine the quantity and distribution of sediment P and in interpretation of chemical factors influencing P release to solution for both physical and chemical phenomena may be influenced by depth of the overlying water.

As an additional guide to the determination of factors influencing elemental transformations in the sediments, a multiple regression model was devised to determine the parameters important to the prediction of total C and total P. All measured parameters were considered except in the case of the prediction of total P for which inorganic P and organic P were omitted. The final results are summarized in Table 60.

Variation in total sediment C could be predicted ($R^2 = 82\%$) using the coefficients of water depth and sediment N content. Thus, total C may be expected to be markedly influenced by these variables. A portion of total P variation ($R^2 = 38\%$) could be predicted using the coefficients of total sediment N and C content. Water depth did not significantly influence the prediction of total P as might be expected from the simple correlation between these two variables (Figure 33). Multiple regression analysis involves the utilization of several parameters which are interrelated and inclusion of N content into the equation negated water depth as a useful parameter. Apparently, variation in N accounted for a major portion of the variation attributed to water depth in simple correlations. It is likely that a water depth-N content interaction term would improve the regression coefficient, however interactions were not considered in this model.

In brief summary, the results indicate that sediment concentrations of C, N and P are not highly variable. Variation in total C, N and P that exists appears at least partially related to sample location and water depth. Furthermore, factors which influence the concentration of C strongly influence N, and to a lesser extent, P.

Table 60. Multiple regression model to predict total sediment carbon and phosphorus contents of Shagawa Lake sediments.

Dependent variable	Intercept	Parameter coefficients[1,2,3]			Multiple correlation coefficient	Variation in total C attributable to parameters
		Depth	N content	C content	(R)	(R^2)
		m	---------%---------		--------------%--------------	
Total carbon	0.461	-0.607	12.638		0.90	82
		±0.150	±1.140			
Total phosphorus	0.077		0.079	-0.0042	0.62	38
			±0.019	+0.0010		

[1] Includes standard error (SE).

[2] Total phosphorus parameter not significant in prediction of total carbon.

[3] Multiple correlation coefficient for total phosphorus model is 0.88 if inorganic phosphorus parameter included.

For future investigations designed to estimate the potential of the sediments to release P to solution prior to and after sewage treatment, sediment samples must be taken which are representative of the lake system within reasonable limits of error. To accomplish this, error due to sampling variation must be known. Furthermore, available information on lake characteristics must be utilized to select sediment samples which are most representative of all the sediments so that the results may be extrapolated to the total lake system. Based on these requirements and the results of statistical analyses outlined above it was recommended that the following samples of Shagawa lake sediments be taken: sample locations (Figure 31) B1b, B5c, B15b, C8b, C12d and E6c.

Except for sample location B15b, locations were randomly selected from categories (Table 61) based on total sediment P concentrations. The coefficient of variation for the categories of sediment total P concentration outlined in Table 61 were approximately 5% compared to a coefficient of variation for total P for all sample locations of approximately 20%. Thus, a stratified random sample design was employed to select the sample locations. A single random sample was selected for each category. Sample location B15b was added to provide representation for the sediments in the deep section at the east end of the lake. Much of the deviation from the mean water depths and C, N and P contents are represented by the sample locations shown.

To achieve a coefficient of variation of <10% for each sample location, it was estimated that 6 replicate samples must be taken through the ice at each location.

The Shagawa Lake sediment samples were subsequently taken in March, 1971 at locations A6d, B13d, B15d, C11d, D8c, and F5a (Figure 31). A total of 6 sediment samples from each location, representing 2-3 dredge loadings per sample, were individually mixed and subsampled in duplicate for analyses of total solids, total P and inorganic P.

The coefficients of variation for total solids, total P (Na_2CO_3 fusion) and inorganic P (H_2SO_4 extraction) ranged from 2.8 to 6.9%, 3.9 to 13.2% and 4.2 to 19.2%, respectively (Tables 62-67). Samples F5a and B13d exhibited the low and high values, respectively, for each of the analyses conducted. Sample F5a was located in a relatively shallow area in which there was little chance for contamination by sewage or mine tailings, whereas the B13d location was deep by comparison

Table 61. Categorization of total phosphorus concentrations in the sediments of Shagawa Lake.

Categories consisting of sediments[1] with total P (μg/g) in the range of								
	900-1000		1100-1300		1300-1500		1500-1700	
	Site	Value	Site	Value	Site	Value	Site	Value
	B1b	1024	A5c	1218	A17b	1368	B13b	1577
	B2c	923	A6d	1130	B5c	1346	B13d	1550
	B3c	1048	A10d	1227	B15a	1303	B15d	1660
	B10c	915	C3a	1208	C11d	1464	C8b	1535
	E10b	942	C8d	1291	C12d	1456		
	F5a	1074	E5b	1211	C15b	1335		
	F9a	1043	E6c	1176	D8b	1368		
	G4c	982	G5a	1154	D8c	1381		
					D11a	1315		
					E7c	1398		
Mean ($\bar{x}$)		994		1202		1374		1581
Standard deviation (Sd)		62		49		54		56
Coefficient of variation (Cv)		6%		4%		4%		4%

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[1] Figure 31

Table 62. Sampling and analytical variability associated with the determination of the forms of phosphorus in sediments (A6d) of Shagawa Lake.

Sample designation	Total solids			Total P			Inorganic P		
	replicates		mean	replicates		mean	replicates		mean
	%			µg/g					
1	9.65	9.93	9.79	993	1010	1002	379	400	390
2	9.81	9.71	9.76	1050	1046	1048	421	418	420
3	10.45	11.09	10.77	886	936	911	399	375	387
4	9.69	9.77	9.73	1083	1036	1060	445	412	428
5	9.60	9.93	9.76	992	984	988	458	441	450
6	9.97	9.77	9.87	1164	1107	1136	382	389	386
MEAN	9.86	10.03	9.95	1028	1020	1024	414	406	410
Standard Deviation	0.32	0.53	0.41	94.5	58.2	76.1	33	23	27
Coefficient of Variation	3.2%	5.2%	4.1%	9.2%	5.7%	7.4%	8.0%	5.7%	6.5%

Table 63. Sampling and analytical variability associated with the determination of the forms of phosphorus in sediments (B13d) of Shagawa Lake.

Sample designation	Total solids replicates		Total solids mean	Total P replicates		Total P mean	Inorganic P replicates		Inorganic P mean
	---------%---------			----------------µg/g----------------					
1	12.89	13.49	13.19	1376	1276	1326	809	746	778
2	11.61	12.28	11.94	1766	1526	1646	1182	969	1076
3	13.03	12.61	12.82	1363	1529	1446	786	941	864
4	12.72	12.85	12.78	1451	1324	1388	850	782	816
5	14.67	14.72	14.70	1130	1053	1092	626	569	598
6	13.15	13.21	13.18	1335	1324	1330	769	744	756
MEAN	13.01	13.19	13.10	1404	1339	1371	837	792	815
Standard Deviation	.98	.86	.91	208	177	181	185	147	157
Coefficient of Variation	7.6%	6.5%	6.9%	14.8%	13.2%	13.2%	22.1%	18.5%	19.2%

Table 64. Sampling and analytical variability associated with the determination of the forms of phosphorus in sediments (B15d) of Shagawa Lake.

Sample designation	Total solids replicates		Total solids mean	Total P replicates		Total P mean	Inorganic P replicates		Inorganic P mean
	%			µg/g					
1	10.48	10.47	10.48	2091	2093	2092	1523	1408	1466
2	9.80	8.47	9.27	1731	1674	1702	1106	1040	1073
3	11.69	10.25	10.99	1676	1969	1822	1135	1285	1210
4	9.76	11.47	10.62	2490	2108	2299	1718	1376	1547
5	9.87	9.98	9.92	1766	2070	1918	1387	1407	1397
6	10.08	10.12	10.10	1749	2070	1910	1390	1340	1365
MEAN	10.28	10.18	10.23	1917	1997	1957	1376	1309	1343
Standard Deviation	.74	.88	.60	317	166	211	232	140	174
Coefficient of Variation	7.2%	8.6%	5.9%	16.5%	8.3%	10.8%	16.9%	10.7%	12.9%

Table 65. Sampling and analytical variability associated with the determination of the forms of phosphorus in sediments (C11d) of Shagawa Lake.

Sample designation	Total solids			Total P			Inorganic P		
	replicates		mean	replicates		mean	replicates		mean
	%			µg/g					
1	12.44	12.93	12.68	1350	1319	1334	787	748	768
2	11.87	12.00	11.94	1510	1429	1470	847	843	845
3	11.71	11.91	11.81	1364	1414	1388	769	802	786
4	11.45	12.11	11.78	1651	1565	1608	962	937	950
5	11.32	11.40	11.36	1614	1623	1618	934	970	952
6	11.46	11.26	11.36	1624	1625	1624	981	964	972
MEAN	11.71	11.94	11.82	1519	1496	1507	880	877	879
Standard Deviation	.41	.59	.49	134	127	128	92	93	91
Coefficient of Variation	3.5%	5.0%	4.1%	8.8%	8.5%	8.5%	10.4%	10.6%	10.3%

Table 66. Sampling and analytical variability associated with the determination of the forms of phosphorus in sediments (D8c) of Shagawa Lake.

Sample designation	Total solids replicates		Total solids mean	Total P replicates		Total P mean	Inorganic P replicates		Inorganic P mean
	--------%	----------	----------	----------	----------	---µg/g---	----------	----------	----------
1	9.01	8.64	8.82	4555	4144	4350	3556	3105	3330
2	9.02	8.57	8.82	4811	4703	4757	3681	3508	3594
3	8.87	8.58	8.72	4330	3981	4156	3426	3078	3252
4	9.76	9.22	9.49	3283	3110	3196	2469	2331	2400
5	9.14	8.61	8.88	4595	4378	4486	3790	3543	3666
6	9.35	8.65	9.00	3961	4019	3990	3177	3212	3194
MEAN	9.20	8.71	8.96	4256	4056	4156	3350	3130	3239
Standard Deviation	.32	.25	.28	557	535	540	481	439	452
Coefficient of Variation	3.4%	2.9%	3.1%	13.1%	13.2%	13.0%	14.4%	14.0%	14.0%

Table 67. Sampling and analytical variability associated with the determination of the forms of phosphorus in sediments (F5a) of Shagawa Lake.

Sample designation	Total solids replicates		Total solids mean	Total P replicates		Total P mean	Inorganic P replicates		Inorganic P mean
	--------%	----------	----------	-----------------	-----------------	--------μg/g	----------	----------	----------
1	9.47	9.25	9.36	1277	1266	1271	603	618	611
2	9.69	9.84	9.76	1163	1121	1142	583	530	556
3	9.40	9.64	9.52	1175	1134	1154	564	530	547
4	9.73	9.98	9.86	1191	1175	1183	568	542	555
5	10.00	10.04	10.02	1164	1176	1170	569	537	553
6	10.28	9.80	10.04	1175	1186	1180	544	573	558
MEAN	9.76	9.76	9.76	1191	1176	1183	572	555	563
Standard Deviation	.33	.29	.27	43	51	46	20	35	24
Coefficient of Variation	3.4%	2.9%	2.8%	3.6%	4.3%	3.9%	3.5%	6.3%	4.2%

and was mottled (red and gray) in appearance reflecting unusual genesis or contamination perhaps by mine tailings. Highest total P values were obtained for two deeper locations in the lake (B15d, D8c). Unusually high total P values (mean 4156 μg/g) were obtained for location D8c which was the deep hole in closest proximity to the sewage outfall.

B. LAKE ERIE

This section summarizes the results of chemical measurements of total, inorganic and organic P and P in inorganic P fractions for sediments from Lake Erie.

Materials and Methods

Sediment sampling sites on Lake Erie are described in Table 68.

Methods employed for the determination of the forms of sediment inorganic P are described in Section IV, A.

Results and Discussion

The results are outlined in Tables 69 and 70.

C. AGENCY LAKE, OREGON

This section summarizes the results of chemical measurements of total, inorganic and organic P and P in inorganic P fractions for sediment from Agency Lake, Oregon.

Materials and Methods

Sediment sampling sites on Agency Lake are described in Table 71.

Methods employed for the determination of the forms of sediment inorganic P are described in Section IV, A.

Results and Discussion

The results are outlined in Tables 72 and 73.

D. DIAMOND LAKE, OREGON

This section outlines the results of investigations to determine (*i*) the mineralogical composition and (*ii*) the total and inorganic P contents for the sediments of Diamond Lake, Oregon.

Table 68. Description of sampling sites on Lake Erie.

Sample designation	Date of collection	Approximate sampling depth		Location
		Sediment	Water	
		cm	m	
G-25-1	7-18-69	0-10	22.8	41° 51.2'N, 81° 26.0'W
I-16-2	7-15-69	0-10	21.3	42° 01.1'N, 82° 11.5'W
I-23-1a	7-15-69	0-10	25.3	42° 02.6'N, 81° 37.5'W
J-21-1	7-16-69	0-10	24.0	42° 09.9'N, 81° 45.1'W
K-28-1	7-17-69	0-10	23.4	42° 14.1'N, 81° 15.3'W
I-23-1b	9-23-69	0-10	25.3	42° 02.6'N, 81° 37.5'W

Table 69. Distribution of organic and inorganic phosphorus in Lake Erie sediments as determined by high temperature ignition methods.

Sample designation[1]	Total P[2]	Inorganic P		Organic P	
		absolute	fraction of total	absolute	fraction of total
	μg/g	μg/g	%	μg/g	%
G-25-1	751	541	72.0	210	28.0
I-16-2	991	782	78.9	209	21.1
I-23-1a	1238	906	73.2	332	26.8
J-21-1	713	528	74.1	185	25.9
K-28-1	782	625	79.9	157	20.1
I-23-1b	713	524	73.4	190	26.6

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[1] Table 68

Table 70. Distribution of phosphorus in inorganic phosphorus fractions of Lake Erie sediments.

Sample designation[1]	P extracted with									
	NH_4Cl (0.5M)	NH_4F (0.5M)	NaOH (0.1M)	NaS_2O_4 $Na_3C_6H_5O_-$	(0.1M) NaOH (0.3M)	HCl			Ignition-HCl (1.0M)	Na_2CO_3 HCl (9.0M)
						(0.5M)	(1.0M)	Total		
I-23-1	4	238	2	278	42	350	49	399	130	93

Table 71. Description of sampling site on Agency Lake, Oregon.

Sample designation	Date of collection	Approximate sampling depth Sediment	Approximate sampling depth Water	Location
		cm	m	
A-1	6-3-69	0-10	1.8	42° 31.5'N, 121° 58.5'W
A-2	7-15-69	0-10	1.8	42° 31.5'N, 121° 58.5'W
A-3	9-8-69	0-10	1.8	42° 31.5'N, 121° 58.5'W
A-4	10-24-69	0-10	1.8	42° 31.5'N, 121° 58.5'W

Table 72. Distribution of organic and inorganic phosphorus in Agency Lake sediments as determined by high temperature ignition methods.

Sample designation[1]	Total P[2]	Inorganic P absolute	Inorganic P fraction of total	Organic P absolute	Organic P fraction of total
	μg/g	μg/g	%	μg/g	%
A-1	475	219	46.1	256	53.9
A-2	725	478	65.9	247	34.1
A-3	426	192	45.1	234	54.9
A-4	675	424	62.8	252	37.2

[1] Table 71

Table 73. Distribution of phosphorus in inorganic phosphorus fractions of Agency Lake sediments.

Sample designation[1]	P extracted[2] with									
	NH_4Cl	NH_4F	NaOH	NaS_2O_4(0.1M)	NaOH	HCl				Na_2CO_3 fusion
	(0.5M)	(0.5M)	(0.1M)	$Na_3C_6H_5O_2$(0.3M)	(1.0M)	(0.5M)	(1.0M)	Total	HCl(1.0M)	HCl(9.0M)
	μg/g									
A-1	<5	71	40	55	7	44	9	53	61	92
A-2	5	51	6	48	21	51	14	65	45	60
A-3	6	62	41	96	36	114	21	135	51	78
A-4	<5	49	60	67	38	185	29	215	52	100

[1] Table 71

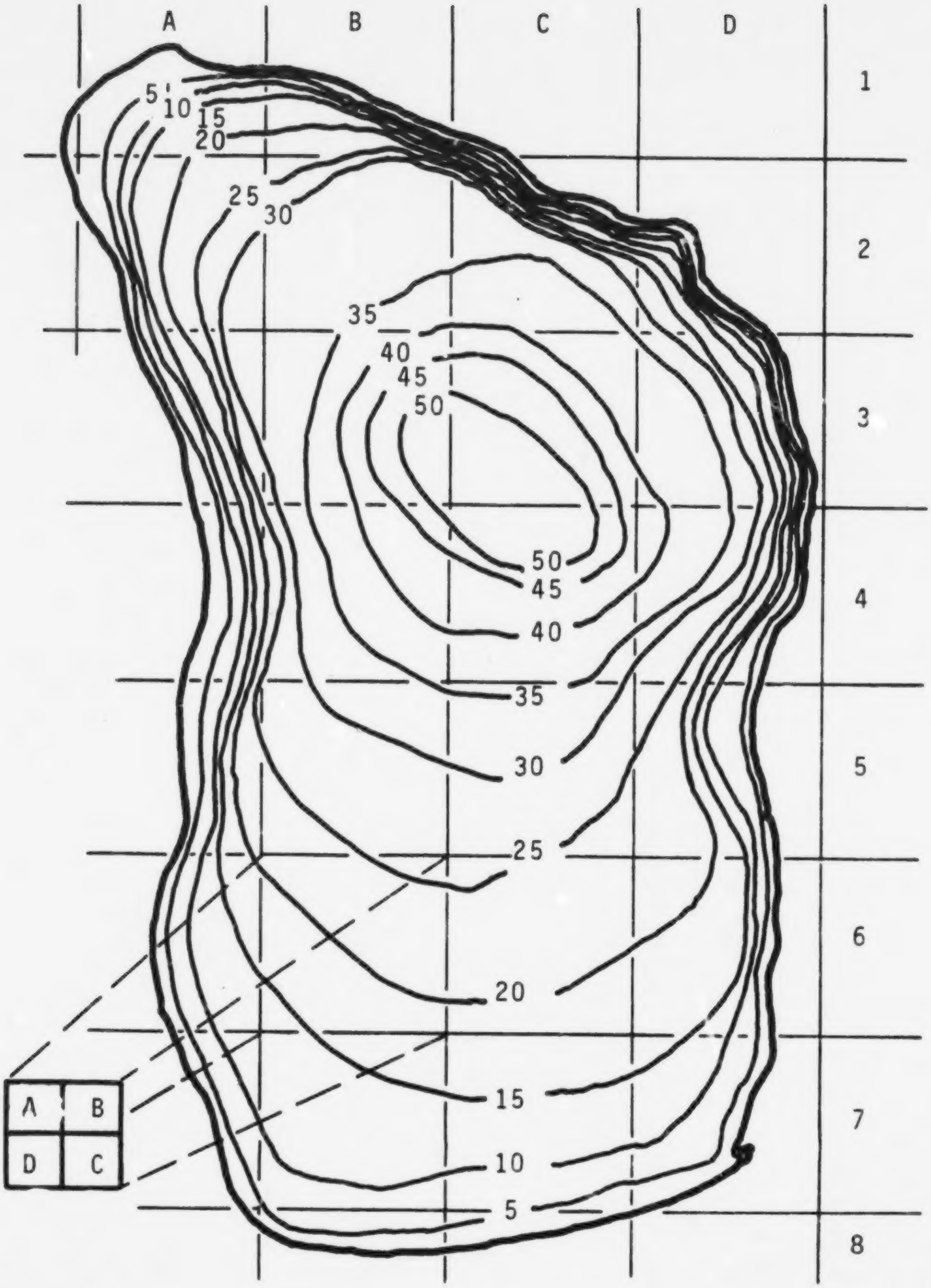
A
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FIGURE 34. GRID SYSTEM - DIAMOND LAKE, OREGON.

Materials and Methods

The Diamond Lake sediment samples (A1c, B2a, B5a, C3d, C6a, D7a) were taken in July, 1971 and designated according to location on the EPA grid system (Figure 34).

Analyses of the mineral composition of the intact sediments were conducted using X-ray diffraction techniques (Section VI, A).

Total sediment P was determined by Na_2CO_3 fusion and inorganic P was estimated by H_2SO_4 extraction as described in Section IV. Organic P was taken as the difference between total and inorganic P.

Results and Discussion

Representative X-ray diffractograms of Diamond Lake sediments are given in Figure 35. Diffraction maxima did not differ significantly with sampling location. The sediments contained relatively low concentrations of crystalline minerals as reflected in the near absence of sharp diffraction maxima. This is in accordance with previous observations that the volume of discrete crystals in ash deposits close to Crater Lake is less than 1% (Williams, 1942). The maxima at a diffraction angle of 28 (3.2 A spacing) are due to residual KCl after treatment. All samples exhibited broad diffraction maxima at diffraction angles (Figure 36) of 22 and 10 (4 and 10 A spacings, respectively). The broad maxima are an indication of a relatively high percentage of amorphous material. Saturation with K tended to sharpen the 10 A maxima, perhaps as the result of the collapse of small quantities of expandable material. In several samples, heating to 500 C reduced the height of the 10 A peak, indicating the presence of endellite. Endellite is a hydrated halloysite mineral known to be present in some volcanic soils. In general, the mineral fraction of the Diamond Lake sediments appears to be derived largely from pumice probably originating from the volcanic eruption of Mt. Mazama.

Total P contents (Table 74) of Diamond Lake sediments ranged from 510 μg/g (A1c) to 994 μg/g (B5a). Although no precise pattern of P distribution with sediment location was apparent, higher P values were generally associated with the northern, deeper portions of the lake. A notable exception was the relatively high P value at the mouth of Camp creek (D7a).

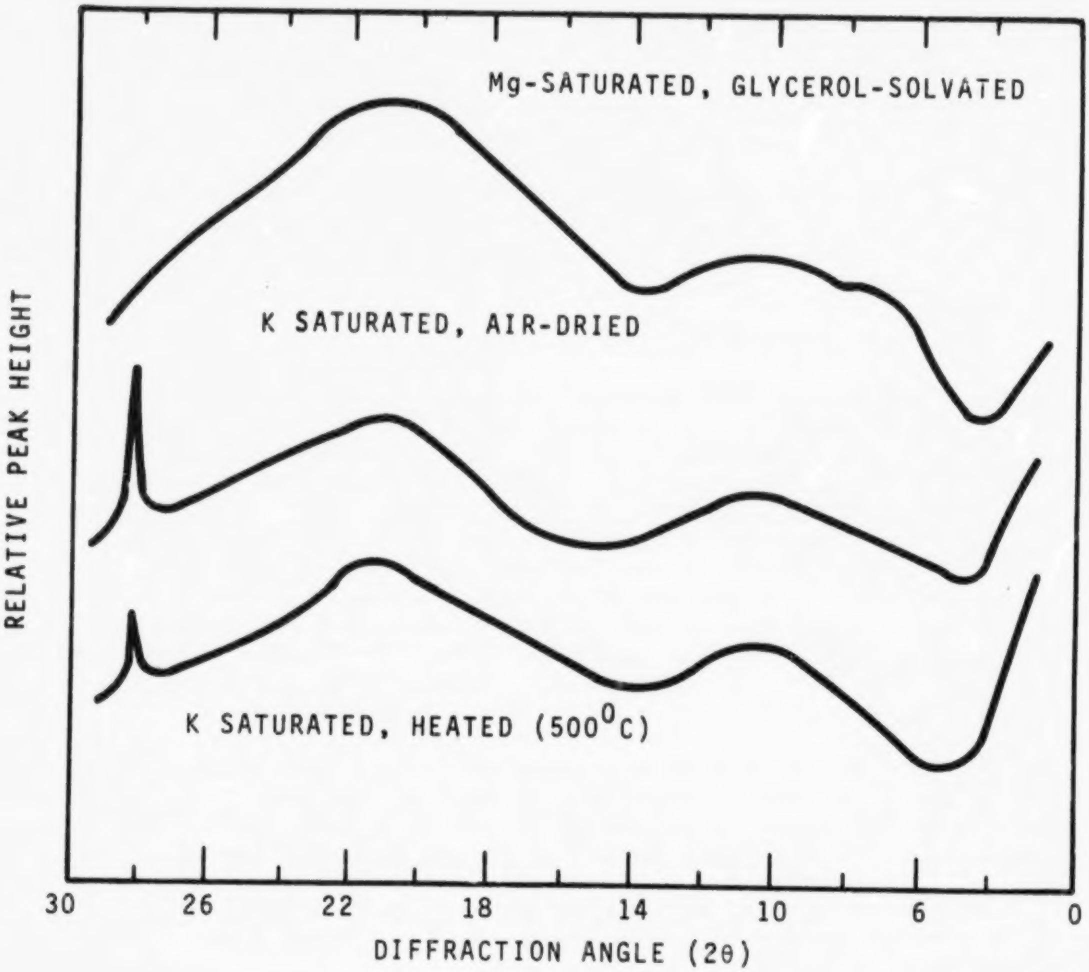

FIGURE 35. REPRESENTATIVE X-RAY DIFFRACTOGRAMS OF CHEMICALLY-TREATED SEDIMENTS FROM DIAMOND LAKE.

Table 74. Total and inorganic phosphorus content of Diamond Lake sediments.

Sample designation	Total solids	Total P	Inorganic P		Organic P	
			Absolute	Fraction of total	Absolute	Fraction of total
	%	μg/g	μg/g	%	μg/g	%
Alc	8.41	510	131	25.7	378	74.3
B2a	6.92	826	302	36.6	524	63.4
B4a	5.68	713	320	44.9	392	55.1
B5a	6.05	994	472	47.5	522	52.5
B6a	8.27	485	99	20.4	386	79.6
B7a	15.12	460	166	36.1	294	63.9
C2c	6.30	759	303	39.9	456	60.1
C3d	5.70	847	368	43.4	480	56.6
C4b	7.51	589	210	35.7	380	64.3
C5a	7.95	483	119	24.6	364	75.4
C6a	8.48	462	106	22.9	356	77.1
C7a	9.32	655	230	35.1	424	64.9
D5a	8.50	466	110	23.6	356	76.4
D7a	23.84	974	585	60.1	388	39.9

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[1] Based on oven dry (60 C) weight

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